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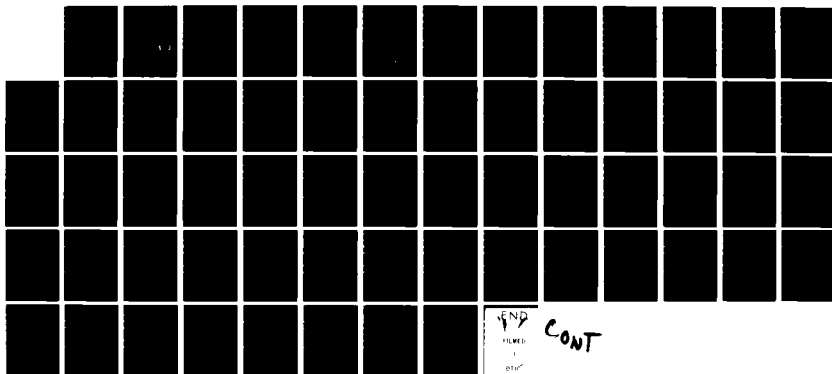
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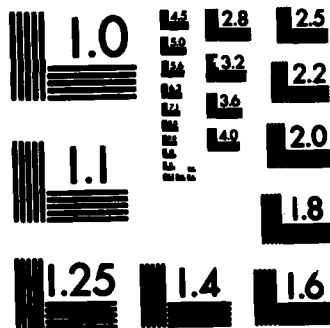
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## Review of Rate Data for Reactions of Interest in HF and DF Lasers

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25 October 1982

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Prepared for  
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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Chemical reactions and energy transfer processes of importance in $H_2-F_2$ and $D_2-F_2$ chemical lasers are reviewed and the current state of knowledge is evaluated. Best current estimates for these processes are given and the uncertainties assessed.  |   |  |

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## I. INTRODUCTION

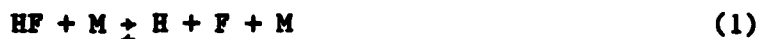
In recent years The Aerospace Corporation's Chemical Kinetics Department, a branch of the Aerophysics Laboratory, has prepared a series of reports that review the kinetics of hydrogen halide lasers (HF, DF, and HCl).<sup>1-4</sup> The most recent of these reports devoted to the HF system was published in June 1978 and covered the literature through September 1977. The most recent DF review was published in August 1977 and covered the literature through 1976. Because the HF and DF reviews were made separately and the results were published in alternate reports, there were occasional inconsistencies between their recommendations. To obviate this regrettable circumstance, we have therefore decided to review the two systems together and present the combined results and recommendations in the present report.

In the format of this report we have not attempted to gather all pertinent data already reviewed in References 1-4. We have concentrated on reporting only the more recent results, but our recommendations are based on all the available literature. Therefore, for the laser scientists whose need is for the best current rate data, the present report will be sufficient until it is superseded by the next review. For the kineticists concerned with more detailed information on particular reactions or energy transfer processes, the earlier reviews may be necessary as well. Lists of recommended rate coefficients for HF and for DF, based on all the literature through April 1981, are given in Appendixes A and B. Appendixes C and D are tables indicating the changes in recommendations that have taken place since the recommendations of References 2 and 4. Appendix E is a table summarizing the current status of knowledge concerning all the reactions, with assessments of the uncertainties in the various rate coefficients.

## II. DISSOCIATION-RECOMBINATION REACTIONS

### A. HF DISSOCIATION

The dissociation of HF was measured in this laboratory by Jacobs, Giedt, and Cohen<sup>5</sup> in 1965. The determination of the rate constant  $k_1$  for the reaction



required a computer program to model the HF infrared emission and relate it to the dissociation process. Also required were the rate coefficients for the other important processes occurring behind the shock, namely, the  $\text{H} + \text{HF}$  exchange reaction and  $\text{H}_2$  dissociation. In Reference 1, the effects of updating the values used for the latter two processes on the determination of  $k_1$  were discussed, and it was concluded that no revisions in the value of  $k_1$  were to be made. In view of the large revisions in the  $\text{H} + \text{HF}$  rate coefficient (Section III), this analysis was repeated again. It was again found that the new calculations made only negligible changes in the determined value for  $k_1$ . Hence, the previous recommendation for that rate coefficient still stands.

### B. DF DISSOCIATION

The dissociation of DF in Ar and He in shock tube experiments was studied by Bott in this laboratory several years ago, but the experimental data were not completely analyzed until recently. The analysis has now been concluded,<sup>6</sup> and the result is that the rate coefficient  $k_2$



for  $\text{M} = \text{Ar}$  is best described by  $k_2 = 2.7 \times 10^{22} T^{-2} \exp(137,130/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at temperatures between 3600 and 7200 K. This yields a recombination rate coefficient that is identical, within experimental error, to that for  $\text{H} + \text{F}$ . A few experiments performed around 5000 K indicate DF dissociation occurs more rapidly in He than in Ar by a factor of  $3.5 \pm 0.5$ .

### C. H<sub>2</sub> and D<sub>2</sub> DISSOCIATION

There have been no new experimental data on these processes. However, the data for H<sub>2</sub> dissociation in the presence of H, H<sub>2</sub>, Ar, and N<sub>2</sub> have been reviewed by Cohen and Westberg<sup>7</sup> and the recommended rate coefficients have been revised very slightly from those given in Reference 2. The current recommendations are given in Appendixes A and B. The D<sub>2</sub> data have not been reexamined, so the previous recommendations still apply.

### D. F<sub>2</sub> DISSOCIATION

The gas-phase dissociation-recombination of F<sub>2</sub> has not been the subject of new studies, but there has been work done on the heterogeneous recombination process.<sup>8,9</sup> The results of the several experimental studies are not in complete agreement, but it does seem that the condition and history of the surface can critically influence the recombination rate.<sup>9</sup> Therefore, it seems unwise to tabulate experimental results that may have been obtained on a poorly characterized surface. Although we did list experimental data in our previous review,<sup>4</sup> laser modelers who find that they may need recombination rate coefficients for a particular experimental facility would be well advised to measure the process in the apparatus of interest rather than rely on data obtained elsewhere that may not really be applicable.

### III. METATHESIS REACTIONS

The status of knowledge concerning the overall reaction rates for all four pumping reactions



has improved considerably since the last reviews in this series. The reactions will be discussed consecutively.

#### A. F + H<sub>2</sub>

In our 1976 review we listed (Table 1) all the experimental data of which we were aware pertaining to the absolute measurement of  $k_3$ ; relative measurements of  $k_3$  were tabulated separately (Table 2), because at the time the absolute measurements were not of themselves sufficiently unambiguous to allow a precise determination of  $k_3$  with great confidence. Since that time, some much more reliable measurements, as well as numerous theoretical calculations, have been published. For completeness, all the absolute experimental measurements not listed in the 1976 review are tabulated here; however, our evaluation rests entirely on the most recent two of these--the measurements of Haidner et al.<sup>10</sup> and of Wurzburg and Houston.<sup>11</sup> In both of these studies, F atoms were produced by multiphoton dissociation of SF<sub>6</sub> and reacted with H<sub>2</sub>, the course of reaction being monitored by observing the time-resolved infrared emission from the product HF. As Fig. 1 shows, the room-temperature determinations of the two studies differ by approximately 25%; the source of this discrepancy has been carefully pursued by the investigators involved, but has not been found. Furthermore, there is a difference in the activation energies reported by the two groups of investigators, but this can be partly accounted for by the existence of curvature in the Arrhenius plot of  $\log k_3$  versus  $1/T$  and the fact that the two studies were conducted over different temperature ranges.

Table 1. Experimental Measurements of  $F + H_2 \rightarrow HF^* + H^a$

| $k = A \exp(-E/RT)$                            |                          | $T$     | $10^{13} k$ (298) | Technique                       |   | Reference       |
|--|--------------------------|---------|-------------------|---------------------------------|---|-----------------|
| $A, \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ | $E, \text{cal mol}^{-1}$ |         |                   | F Atom Source                   | Detection Method                                      |                 |
|  |                          | 298     | $1.5 \pm 0.4$     |                                 | Molecular beam mass spectrometry                      | 12              |
| $1.6 \times 10^{14}$                           | 1200                     | 250-375 | 2.1               | $F_2$ discharge                 | $H_2$ consumption by mass spectrometry; F atom excess | 13              |
| $1.1 \times 10^{14}$                           | 1050                     | 260-370 | 1.9               | $F_2$ discharge                 | $H_2$ consumption by mass spectrometry; $H_2$ excess  | 13              |
| $2.3 \times 10^{14}$                           | 1550                     | 298-397 | 1.65              | $N + NF_2$                      | Mass spectrometry                                     | 13 <sup>b</sup> |
|  |                          | 298     | 2.4               | $NF_3$ discharge                | $NF$ laser emission pulse width                       | 14              |
|  |                          | 300     | 0.14              | $SF_6$ discharge                | $HF$ chemiluminescence                                | 15              |
|  |                          | 298     | $1.0 \pm 0.08$    | $F_2$ thermal dissociation      | ESR   | 16              |
| $5.5 \times 10^{13}$                           | $512 \pm 199$            | 150-300 | 2.3               | $CF_4$ discharge                | ESR   | 17              |
|  |                          | 298     | 1.3               | $MoF_6$ flash photolysis        | $HF$ laser emission                                   | 18              |
|  |                          | 298     | 2.1               | $SF_6$ multiphoton dissociation | $HF$ chemiluminescence                                | 19              |
|  |                          | 298     | $2.0 \pm 0.3$     | $SF_6$ multiphoton dissociation | $HF$ chemiluminescence                                | 20              |
| $(1.3 \pm 0.25) \times 10^{14}$                | $1182 \pm 100$           | 295-765 | $1.8 \pm 0.3$     | $SF_6$ multiphoton dissociation | $HF$ chemiluminescence                                | 10              |
| $6 \times 10^{13}$                             | $860 \pm 100$            | 190-373 | 1.4               | $SF_6$ multiphoton dissociation | $HF$ chemiluminescence                                | 11              |

<sup>a</sup>Results not cited in Reference 1. All values are as reported; no recalculations or reevaluations have been made.

<sup>b</sup>Results of Reference 34, reanalyzed in Reference 22.

Table 2. Experimental Measurements of  $F + D_2 \rightarrow DF^* + D^a$

| $k = A \exp(-E/RT)$                              |                                     | $T$     | $10^{13}k$ (298) | Technique  |                               | Reference |
|--|-------------------------------------|---------|------------------|--|-------------------------------|-----------|
| $A, \text{cm}^3 \text{mol}^{-1} \text{sec}^{-1}$ | $E, \text{cal mol}^{-1}$            |         |                  | F Atom Source                                    | Detection Method              |           |
| (Relative measurement)                           | $5.7 \pm 3.7 \times 10^{13}$<br>2.4 | 298     | 1.9              | $\text{NF}_3$ discharge                          | DF laser emission pulse width | 21        |
|  |                                     | 273-457 |                  | Nuclear rf coil $^{19}\text{F}(m, 2n)18\text{F}$ | Radio assay                   | 22        |
|  |                                     | 150-300 | 2.2              | $\text{CF}_4$ discharge                          | ESR                           | 17        |
|  |                                     | 298     | $1.2 \pm 0.18$   | $\text{SF}_6$ multiphoton dissociation           | DF chemiluminescence          | 20        |
| $6.4 \times 10^{13}$                             | $1200 \pm 142$                      | 295-678 | $9.5 \pm 1.7$    | $\text{SF}_6$ multiphoton dissociation           | DF chemiluminescence          | 10        |
| $5.5 \times 10^{13}$                             | $1100 \pm 100$                      | 190-373 | $8.5 \pm 1.8$    | $\text{SF}_6$ multiphoton dissociation           | DF chemiluminescence          | 11        |

<sup>a</sup> Results not cited in Reference 2. All values are as reported; no recalculations or reevaluations have been made.

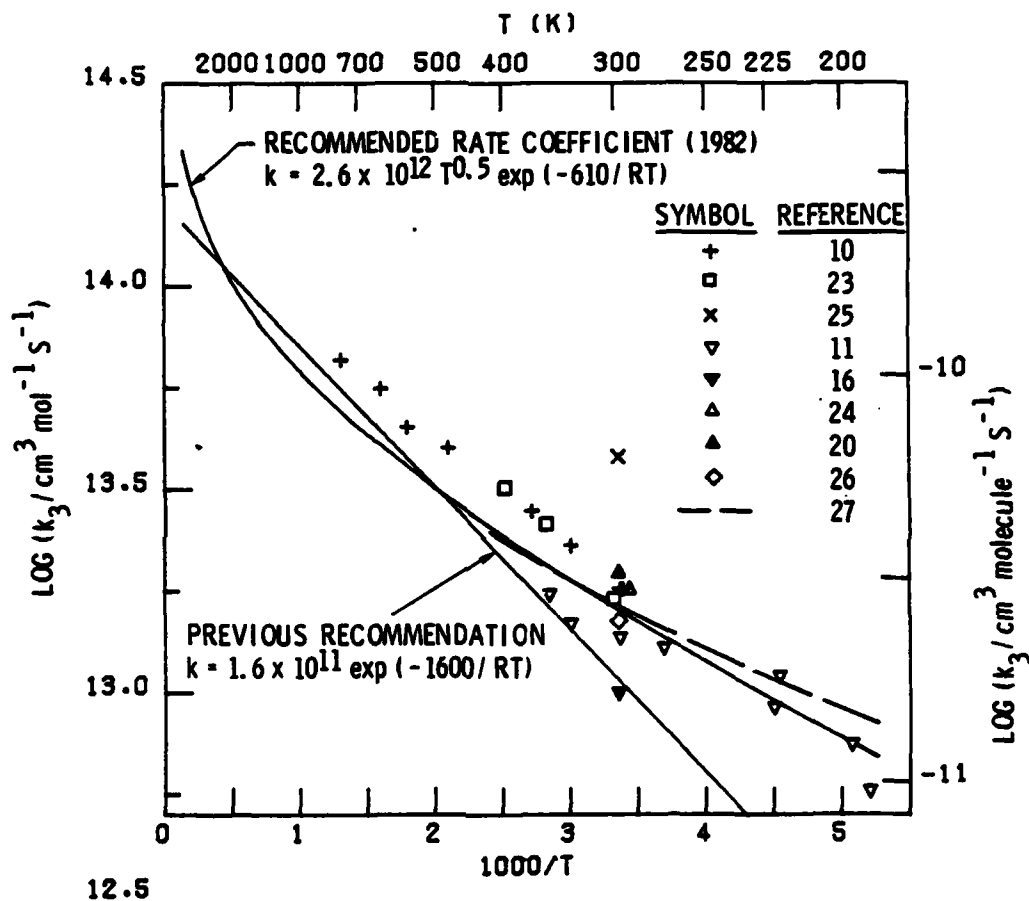


Fig. 1. Rate Coefficient for  $F + H_2$ . Experimental data and old and new recommended expressions.

An extensive series of transition-state theory calculations has been carried out by Westberg and Cohen,<sup>28</sup> who conclude that the best expression consistent with both the experimental data and the best theoretical calculations of the geometry of the transition state is  $k_3 = 2.6 \times 10^{12} T^{0.5} \exp(-610/RT)$   $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$  over the temperature range of 200 to 2000 K. This yields a value for  $k_3$  larger than the 1978 recommended value by approximately 50% at 300 K, but within 15% of it in the range of 1000-2000 K.

There has been one significant remeasurement of the HF product state distribution in this pumping reaction since our 1978 review. Bittenson et al.<sup>29</sup> developed a modification of Polanyi's arrested relaxation technique<sup>30</sup> designed to permit lower flows and time dependence measurements of the emission spectra. In this way, corrections for secondary processes could be made. Their results differ negligibly from those of Perry and Polanyi,<sup>31</sup> on which our 1978 recommendation was based. Hence, we recommend again the values obtained by Perry and Polanyi, except that, following the suggestion of the theoretical trajectory calculations of Wilkins,<sup>32</sup> we assume no direct population of the  $v = 0$  level. Thus, the recommendations are:  $k_3(1):k_3(2):k_3(3) = 0.15:0.55:0.30$ . As before, we assume that these ratios are temperature independent, though we add that this assumption is not firmly grounded in experimental evidence.

#### B. F + D<sub>2</sub>

The potential energy surface for this reaction is the same as that of reaction 1. On the basis of transition-state theory calculations performed using this potential energy surface and taking into account the recent, reliable experimental data of Heidner et al.<sup>10</sup> and of Wurzberg and Houston,<sup>11</sup> Westberg and Cohen<sup>28</sup> concluded that the best expression for  $k_4$  is  $2.0 \times 10^{12} T^{0.5} \exp(-830/RT)$   $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$  for  $200 < T < 2000$  K. The two most reliable experimental determinations of  $k_4$  are those of Heidner et al. and of Wurzberg and Houston. These experiments were carried out in the same facilities as were used to measure  $k_3$ ; however, in this case there is no discrepancy between the room-temperature results of the two studies. These results, as well as others published since our 1977 review, are listed in Table 2 and



plotted in Fig. 2. The recommended expression yields values for  $k_4$  very similar to those of the 1977 recommendation near 300 K, but smaller by approximately a factor of 2 in the range of 1000-2000 K. Both the new and the old recommendations are shown in Fig. 2.

The DF vibrational distribution in this reaction has been remeasured recently by Bittenson et al.,<sup>29</sup> who obtained nearly the same results, within experimental uncertainty, as did Perry and Polanyi.<sup>31</sup> We retain the recommendation of our last review, which was based on the experimental results of Perry and Polanyi at 300 and 1130 K.

### C. H + F<sub>2</sub>

The recommendation in our previous reviews was based on the experimental work of Albright et al.<sup>33</sup> Since then, another experimental study was published by Homann et al.<sup>34</sup> These workers, like the earlier ones, used a discharge flow system with mass spectrometry to monitor reagent and product concentrations. However, Homann et al. did not sample from the mixing region, thus avoiding one experimental difficulty of the earlier study; their results therefore seem to be more reliable and yield values of  $k_5$  approximately a factor of 2 lower than those of Albright et al. They obtained  $k_5 = (4 \pm 1) \times 10^{13} \exp(-2187/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . A single room-temperature measurement relative to the rate of H + Cl<sub>2</sub> has also been reported by Sung et al.,<sup>35</sup> but they are dubious of their absolute accuracy.

Westberg and Cohen<sup>28</sup> have carried out transition-state theory calculations for  $k_5$  and determined that for any reasonable geometry of the transition state there will be curvature in the Arrhenius plot. They conclude, on the basis of experimental results of Homann et al. and on their own calculation, that the best expression for  $k_5$  is  $3.0 \times 10^9 T^{1.5} \exp(-1680/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  over the temperature range of 200 through 2000 K. The uncertainty in  $\log k_5$  is approximately  $\pm 0.3$  throughout the experimental temperature range of 220 through 500 K, increasing to  $\pm 0.5$  at 2000 K. Thus, the recommended value of  $k_5$  is smaller than the 1978 recommendation by a factor of 2.3 at 300 K and larger at 2000 K by a factor of 2.7. Both recommendations, as well as experimental data, are shown in Fig. 3.

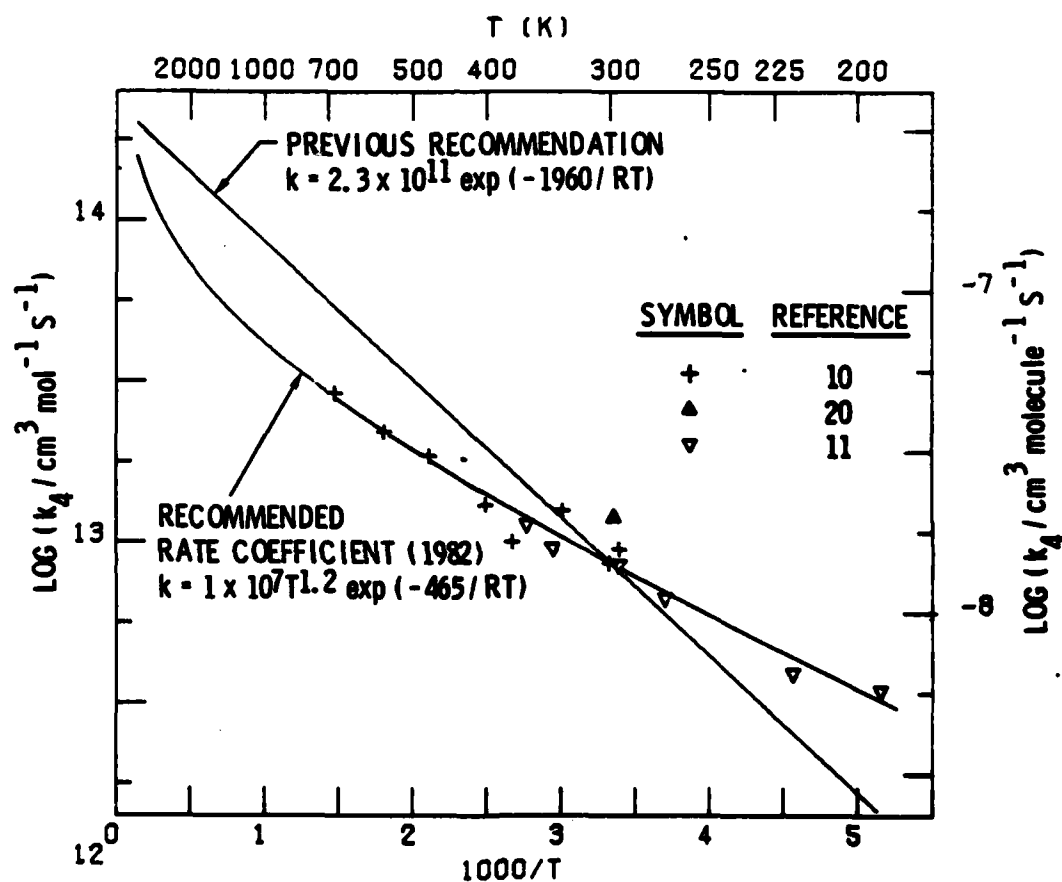


Fig. 2. Rate Coefficient for  $F + D_2$ . Experimental data and old and new recommended expressions.

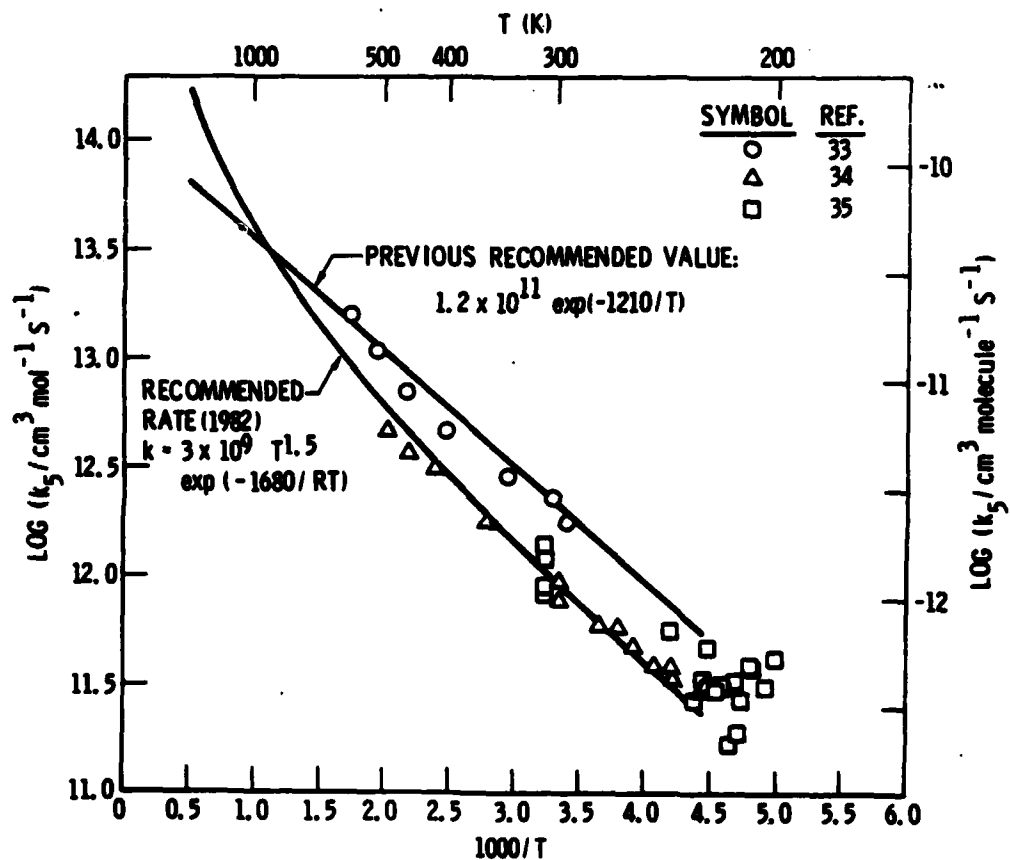


Fig. 3. Rate Coefficient for  $\text{H} + \text{F}_2$ . Experimental data and recommended expressions.

The recommendations for vibrational distribution given in our 1976 review were based on the experimental results of Polanyi and Sloan,<sup>36</sup> but were modified by what were then believed to be the best values for the HF Einstein coefficients. With those modifications, it appeared that less than 5% of the nascent HF(v) was produced in vibrational levels above  $v = 6$ . Since the trajectory calculations of Wilkins<sup>37</sup> suggested no direct population of such high vibrational levels, it was assumed that the observations could be accounted for by vibrational relaxation. More recently, however, Jakubetz<sup>38</sup> pointed out an error in the Einstein coefficient corrections, so that in fact the experimental results suggest as much as 25% of the nascent HF is produced in  $v = 7$  and 8. Sung et al.<sup>35</sup> reported vibrational distributions very similar to those of Ref. 36 except for the absence of any HF(8). Bittenson et al.<sup>29</sup> performed computer modeling calculations indicating that under experimental conditions of Polanyi and Sloan there would indeed have been some vibrational relaxation prior to the observations being made, the effect of which would be to form more low-vibrational-level HF than was originally produced in the  $H + F_2$  reaction. However, it seems less likely that secondary processes could produce high vibrational levels where they did not already exist. It seems, therefore, that the experimental results of Polanyi and Sloan,<sup>36</sup> corrected with Einstein coefficients of Sileo and Cool,<sup>39</sup> are to be preferred over the trajectory calculations. Thus, we recommend the following distribution numbers:

| $k_5(0)$ | $k_5(1)$ | $k_5(2)$ | $k_5(3)$ | $k_5(4)$ | $k_5(5)$ | $k_5(6)$ | $k_5(7)$ | $k_5(8)$ |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 0        | 0        | 0        | 0.07     | 0.10     | 0.23     | 0.33     | 0.15     | 0.12     |

The small quantities of HF(1) and HF(2) observed are attributed to secondary processes. In any case, the amounts produced are negligible compared to the effects of reaction (3). It has previously been assumed that these distribution numbers were temperature independent, and there is no more recent information that would support altering this assumption.

#### D. D + F<sub>2</sub>

There are no experimental measurements of  $k_6$ . However, the same transition-state model appropriate for the H + F<sub>2</sub> reaction should be applicable for this reaction as well; consequently,  $k_6$  can be predicted from the experimental results for  $k_5$ . Westberg and Cohen<sup>28</sup> discussed this problem and carried out transition-state theory calculations for both reactions. They concluded that the best estimate for  $k_6$  is  $2.0 \times 10^9 T^{1.5} \exp(-1650/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  over the temperature range of 200 through 2000 K, with an uncertainty in log  $k_6$  of approximately  $\pm 0.3$  up to 500 K, increasing to  $\pm 0.6$  at 2000 K. This expression gives recommended values for  $k_6$  smaller than the 1977 recommendation by approximately 30% at 300 K and larger at 2000 K by a factor of 3.6. Both recommendations are shown in Fig. 4.

Until very recently, the vibrational distribution for this reaction had not been measured directly, and recommendations were based on results for the H + F<sub>2</sub> reaction, properly scaled to take into account the difference in vibrational frequencies for the two product molecules. Now there are two reports of experimental determinations.

Jonathan et al.<sup>40</sup> used the measured relaxation infrared chemiluminescence method which had been used in the same laboratory eight years ago for H + F<sub>2</sub>. They observed DF(v) in vibrational levels 2 to 12, with the v = 10 level the most heavily populated. Bittenson, Tardy, and Wanna<sup>29</sup> have used their new technique, called chemiluminescence mapping, referred to in Section III.A. In this procedure, D<sub>2</sub> gas is passed through a cooled microwave cavity to produce D atoms, which are then mixed with flowing F<sub>2</sub>, the flow of which can be pulsed with a mechanical chopper. Emission intensity is monitored at six downstream positions, at each of which a spectral scan is made. By repeatedly pulsing and adding the optical signals with an optical multichannel analyzer, Bittenson et al. were able to operate at considerably lower flow rates (and pressures) than were previously used in the measured relaxation or arrested relaxation techniques: typical operating conditions for their experiments were 0.1 to 1 mTorr, F<sub>2</sub>:H<sub>2</sub> ratios of 50 and 5000; and dissociation of H<sub>2</sub> ranging from 1% to 90%. These refinements were apparently successful in

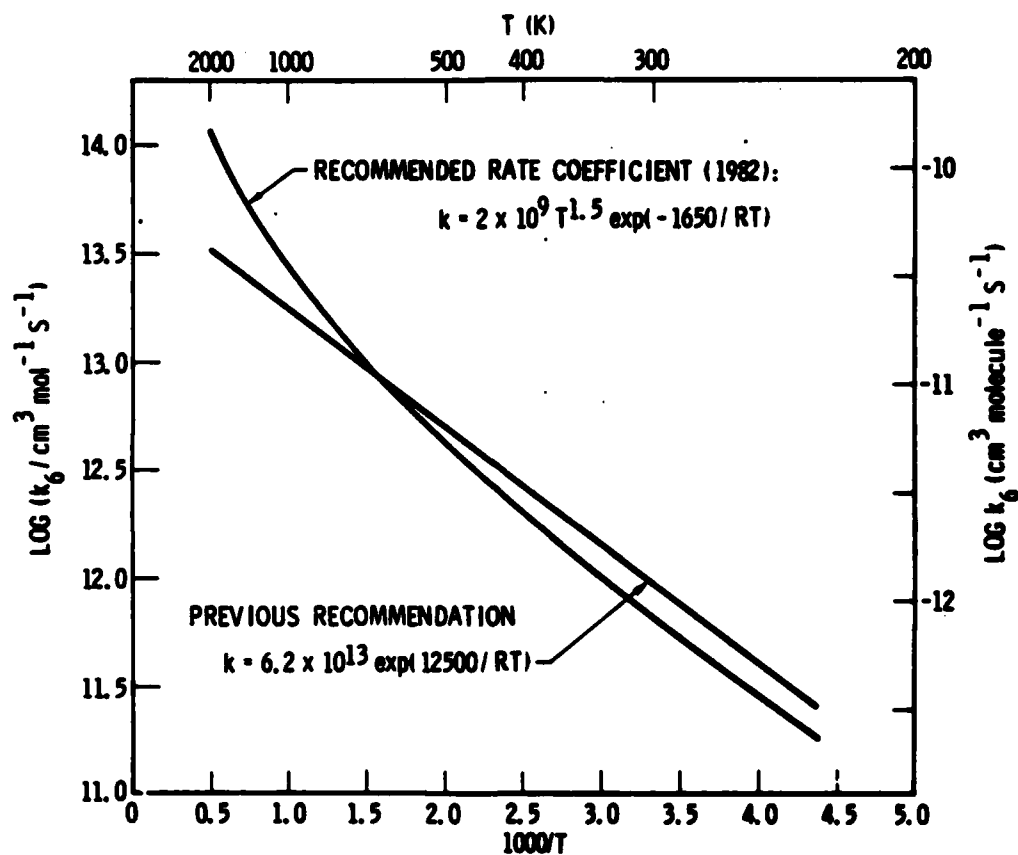


Fig. 4. Rate Coefficient for  $\text{D} + \text{F}_2$ . Experimental data and recommended expressions.

eliminating secondary reactions, and the product distribution observed was quite narrow: only  $v = 10$  through  $13$  were observed, with the population peaking at  $v = 11$ . Their results are compared with those of Jonathan et al. in Table 3.

Table 3. Experimental Measurements of  $D + F_2$  Vibrational Distribution of  $DF(v)$

| $v$ | Jonathan et al. <sup>40</sup> | Bittenson et al. <sup>29</sup> |
|-----|-------------------------------|--------------------------------|
| 2   | 0.01                          | 0                              |
| 3   | 0.02                          | 0                              |
| 4   | 0.02                          | 0                              |
| 5   | 0.04                          | 0                              |
| 6   | 0.04                          | 0                              |
| 7   | 0.10                          | 0                              |
| 8   | 0.14                          | 0                              |
| 9   | 0.20                          | 0                              |
| 10  | 0.24                          | 0.05                           |
| 11  | 0.15                          | 0.51                           |
| 12  | 0.06                          | 0.29                           |
| 13  | 0                             | 0.15                           |

A comparison of the methods and results suggests that, in the results of Jonathan et al.,<sup>40</sup> there is already a considerable secondary reaction producing a much wider distribution of product states. The narrow distribution observed by Bittenson et al.<sup>29</sup> is in qualitative agreement with theoretical calculations of Wilkins,<sup>37</sup> but the observed levels are shifted upward (calculations indicate  $DF$  is formed from  $v = 5$  through  $9$ ). This suggests that

the  $D + F_2$  reaction is significantly more efficient at converting chemical to vibrational energy than is  $H + F_2$ , but the reason for this difference is not apparent. Nevertheless, the results of Bittenson et al. are the best information presently available, and we recommend their distribution numbers.



#### IV. ENERGY TRANSFER PROCESSES

There are two persistent problem areas in HF vibrational relaxation: (1) relaxation by H atoms, and (2) self-relaxation by a combination of V-V and V-R,T energy transfer. These processes continue to demand attention because (1) they are the fastest deactivation processes in the HF system and, therefore, are principal factors in the loss of laser power; and (2) they are the most difficult to resolve experimentally, particularly when upper vibrational levels of HF are involved. Recent studies in both areas will be used as guides to the rate coefficients.

Vibrational energy transfer studies involving DF, though extensive, have lagged behind HF studies to some extent. Insights can sometimes be gained by examination of the relevant HF data for analogous processes. We have not attempted a critical evaluation of the theoretical calculations that have been published. In the cases where experimental evidence seems so firm as to leave little room for doubt, theoretical predictions have been ignored. Theoretical results are discussed only where experimental data are insufficient or completely lacking.

Most experimental investigations result in the measurement of an exponential relaxation time  $\tau$  at a given pressure  $p$  and temperature  $T$ . In order to convert this relaxation time to a rate coefficient  $k$  in units of  $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ , certain assumptions concerning the nature of the relaxation process must be made. According to the harmonic oscillator model

$$p\tau = \frac{RT}{k_{(1,0)} - k_{(0,1)}} = \frac{RT}{k_{(1,0)} [1 - \exp(-\Delta E/RT)]}$$

where  $k_{(1,0)}$  is the rate coefficient for the deactivation of the  $v = 1$  level to  $v = 0$ ,  $k_{(0,1)}$  the rate coefficient for the reverse reaction,  $\Delta E$  the exothermicity of the reaction, and  $R$  the universal gas constant.

This formulation, which has been used by all experimentalists to deduce rate coefficients from their measurements, is strictly accurate only for a harmonic oscillator, which HF and DF are not. However, the deviation because of anharmonicity does not have a serious effect. More important is the implicit assumption that the vibrational states involved are rotationally equilibrated. While this assumption is valid for all of the nonlasing experiments in which rate coefficients have been measured, it is probably not valid in many lasing systems.

In the following paragraphs, different chaperones are treated, and an analytical expression has been fitted to the results of each experimental study where the deactivation reactions were studied over a range of temperatures.

#### A. HF SELF-RELAXATION

There are no new data that would change the previous recommendation<sup>4</sup> for the rate coefficient for the deactivation process



However, both theoretical and experimental studies of upper vibrational level deactivation have been published.<sup>41-45</sup> An important conclusion of the separate trajectory calculations of Wilkins<sup>41</sup> and Billing and Poulsen<sup>42</sup> is that, in the collision between two HF molecules, one of which is vibrationally excited, a favored process is the internal conversion of vibrational-to-rotational energy, with negligible energy being transferred to the collision partner. This result is consistent with arguments by Chen and Moore<sup>46</sup> on the basis of experimental data for HCl and DCl. An important difference in the conclusions of the two theoretical studies is that Wilkins found multiquantum transitions to represent a large fraction of the V-R,T deactivation of the upper levels, whereas Billing and Poulsen found them to be unimportant. Both studies showed V-V transitions to be primarily single-quantum processes. One of the primary differences between the two calculations was the well depth of 6.3 kcal/mol used by Billing and Poulsen, compared to the value of 2.7 kcal/mol used by Wilkins. The effect of the value of the well depth on the results is currently being explored by Wilkins.

Experimental studies of HF self-relaxation of the upper vibrational levels have been performed at room temperature near 295 K. Douglas and Moore<sup>45</sup> used a pulsed dye laser to pump a small fraction of HF to HF(4) and monitored the decay of the HF(4) and HF(3) fluorescence. They determined the rate coefficients for the deactivation of HF(4) and HF(3) from the measured decay times. By comparing the fluorescence intensities of the two vibrational states, they concluded that the single-quantum processes



accounted for at least 90% of the deactivation of  $v = 4$ .

The separation of the total rate into V-V and V-R,T contributions is more difficult. In general, the rate of energy transfer decreases as the magnitude of vibrational energy converted to translational energy increases; consequently, V-V energy transfer, in which only a small surplus of energy is transformed to translational energy, is generally much faster than V-R,T transfer. In the case of homonuclear diatomics, the ratio of V-T to V-V transfer rates is generally several orders of magnitude; HF and DF are unusual in that the difference between their V-T and V-V rates is only one order of magnitude. This anomaly makes the experimental separation of V-V from V-T processes difficult. Our recommendations in this review will rest partly on theoretical calculations and partly on an analogy of HF self-deactivation rates to HF-diatomic molecule deactivation rates.

In Fig. 5 we have plotted the deactivation rate coefficients, measured near room temperature, versus  $v$ . Bott<sup>47</sup> has postulated that several sets of HF and DF relaxation data obtained by Poole and Smith<sup>48,49</sup> are systematically low by factors of about 2. On this basis their rate coefficients for HF self-relaxation were multiplied by a factor of 2.1. Of the several techniques of upper vibrational level deactivation,<sup>44-55</sup> the dye laser pumping technique<sup>44,45</sup> is the most direct and the simplest to interpret for  $v > 2$ . The separation of the rate coefficients into V-V and V-R,T contributions is not so

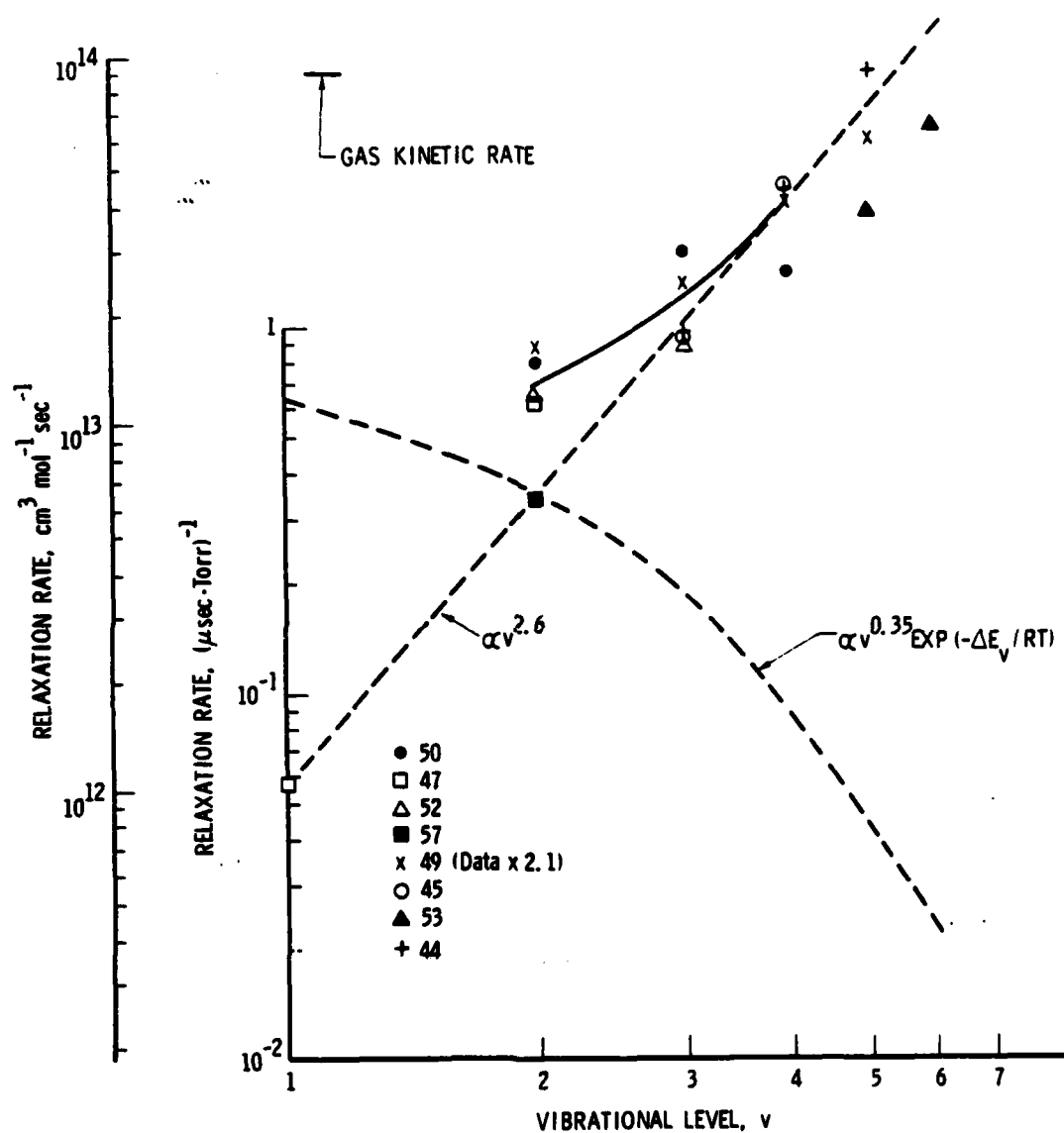


Fig. 5. HF Self-Relaxation Rates Plotted versus Vibrational Level. ( $T = 295 \text{ K}$ ).

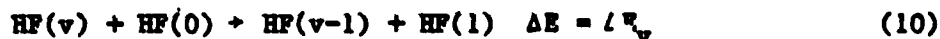
straightforward, and we have to use theoretical results and analogies to other experimental results as a guide.

Recent experimental studies of HF(v)<sup>56</sup> and DF(v)<sup>47</sup> deactivation by diatomic molecules indicate that the deactivation rates scale as  $v^{2.7 \pm 0.2}$  for HF(v) and  $v^{1.9 \pm 0.1}$  for DF(v) when the process is exothermic. The  $v$  scaling appears to be independent of the collision partner and dependent only on the nature of the excited molecule, HF(v) or DF(v). For instance, the deactivation rates of DF(v) scale the same in H<sub>2</sub>, N<sub>2</sub>, and HF. This evidence suggests that the rate coefficients for the exothermic V-R,T deactivation of HF(v) by HF should scale as  $v^{2.7 \pm 0.2}$ . Indeed, a  $v^{2.6}$  scaling of the  $v = 1$  data gives a good fit to the high  $v$  data in Fig. 5. The filled square for  $v = 2$  in Fig. 5 is the value deduced by Cohen and Bott<sup>57</sup> from pulsed laser experiments for the V-R,T deactivation rate of HF(2). It is also in good agreement with the proposed scaling of the V-R,T rate coefficients. Recent measurements by Jursich and Crim<sup>44</sup> of  $v = 4,5,6$  deactivation fall very close to a  $v^{2.7}$  scaling. Like the other experimental measurements, these phenomenological rates reflect the sum of all deactivation mechanisms.

The rate coefficient for the V-V exchange



can be determined from Fig. 5 by subtracting the V-R,T contribution from the best value of the data for the total rate coefficient. Figure 5 shows the V-V and V-R,T contributions to be about equal for  $v = 2$ , with values of about  $0.35 (\mu\text{Torr})^{-1}$  or  $6.5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , giving a total deactivation rate of  $0.70 (\mu\text{Torr})^{-1}$  or  $1.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The extrapolation of the V-V rate to higher vibrational levels is somewhat uncertain. Wilkins<sup>41</sup> and Billing and Poulsen<sup>42</sup> found the V-V rate coefficients for the endothermic exchanges



to decrease with  $v$  near room temperature. The rate coefficients of Billing and Poulsen<sup>42</sup> increase with  $v$  for  $v = 2, 3$ , and 4 at somewhat higher temperatures. Wilkins<sup>41</sup> found the rate coefficients to decrease with  $v$  even for the exothermic exchanges ( $-10$ ), with the rate coefficients decreasing as  $(1.81)^{1-v}$ . Qualitatively, the V-V rates can be expected to decrease, at least at low temperatures, because of their increasing endothermicity. According to both theoretical studies, the V-V exchange rate extrapolates to only small contributions to the total deactivation rate of the high vibrational levels.

In Fig. 5 we have assumed the rate coefficient for the exchange (10) to be proportional to  $v^{0.35} \exp(\Delta E_v/RT)$ , where  $\Delta E_v$  is the exothermicity of the exchange. [The values of  $\Delta E_v$  are negative for the endothermic exchange (10).] This dependence is a compromise between the theoretical results of Wilkins<sup>41</sup> and Billing and Poulsen;<sup>42</sup> it is also the  $v$  dependence of HF( $v$ ) deactivation by H<sub>2</sub>.<sup>48,56</sup> The deactivation of HF( $v = 1,2,3$ ) by H<sub>2</sub> occurs primarily by V-V exchanges if the present understanding is correct (Section IV.C.1), and these exchanges have energy mismatches that increase with  $v$  by approximately the same amount as the HF( $v$ )-HF(0) exchanges. The solid curve in Fig. 5 is the sum of this V-V rate coefficient and the V-R,T rate coefficient and is a reasonable fit to the data. In a study of

$$DF(2) + DF(0) \frac{k_{11}}{k_{-11}} DF(1) + DF(1) \quad (11)$$

Bott<sup>58</sup> found  $k_{11} \propto T^{-1} \exp(-\Delta E_{11}/RT)$  for the endothermic rate coefficient which implies  $k_{-11} \propto T^{-1}$  for the exothermic exchange rate. The  $T^{-1}$  temperature dependence of  $k_{-11}$  is characteristic of HF(1)-HF, DF(1)-DF, and DF(1)-HF V-R,T deactivation processes, all of which are exothermic. Therefore, we suggest for the V-V exchanges (10) rate coefficients of

$$k_v = 3.6 \times 10^{15} T^{-1} v^{0.35} \exp(\Delta E_v/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Our recommended rate coefficients for HF and DF self-deactivation by V-R,T processes reflect the results of experiments in nonlasing systems. Under such conditions, in which the various vibrational states are in

rotational equilibrium, the plots of  $k$  versus  $1/T$  indicate a minimum (at about 1300 K for HF and for DF). Detailed state-to-state rate coefficients obtained by Wilkins<sup>41</sup> with trajectory calculations increase monotonically with  $T$ . Wilkins and Kwok<sup>59</sup> have argued that the minima in the plots of rate coefficients versus  $T$  occur because the empirical V-R,T process is actually a complex combination of many V-R,T and R-R processes. Thus, the recommended rate coefficients may not be valid when rotational states are not equilibrated.

## B. DF SELF-RELAXATION

The deactivation process



has been studied by a number of independent investigators in the temperature range of 200 to 5000 K. The data are shown in Fig. 1 of Reference 2 and are fitted reasonably well by the expression  $k = (10^{14.9} T^{-1.3} + 10^{4.05} T^{2.37}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

The total rate coefficient for the sum of the two deactivation processes

$$\text{DF}(2) + \text{DF}(0) \rightarrow \text{DF}(1) + \text{DF}(1) \Delta E = 91.6 \text{ cm}^{-1} \quad (13a)$$

$$+ \text{DF}(1) + \text{DF}(0) \quad (13b)$$

has been studied<sup>58</sup> between 295 and 720 K. Self-deactivation studies for  $v > 2$  have not been performed. Theoretical calculations and experimental studies of similar processes in HF and DF can serve as a guide. For instance, the deactivation rates<sup>47</sup> of  $\text{DF}(v)$  by  $\text{H}_2$ ,  $\text{N}_2$ , and HF scale as  $v^{1.9 \pm 0.1}$ , suggesting that the rate coefficients for the exothermic V-R,T deactivation of  $\text{DF}(v)$  by DF should also scale as  $v^{1.9 \pm 0.1}$ .

Similar arguments were used in the previous section for HF self-relaxation. The question of single or multiquantum transitions is an important one. Although the calculations of Wilkins predicted that multiquantum transitions are important in DF V-R,T self-relaxation,<sup>60</sup> as well as in HF V-R,T

self-relaxation,<sup>41</sup> those of Poulsen and Billing<sup>42,61</sup> for HF(v)-HF, HF(v)-DF(0) and DF(v)-HF(0) deactivation predicted single-quantum transitions. On the basis of the Douglas and Moore<sup>45</sup> experiment, we chose single-quantum transitions for HF, and it would seem appropriate to do the same for DF. Therefore, for the process



we would suggest  $k_v = v^{1.9} (10^{14.9} T^{-1.3} + 10^{4.05} T^{2.37}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

The rate coefficient for V-V exchange between DF(2) and DF(0) (process 13a) can be estimated from the total rate measurements and the V-R,T rates scaled as  $v^{1.9}$  to  $v = 2$ . The total rate coefficient at 295 K was found to be  $0.73 (\mu\text{s Torr})^{-1}$  by Bott<sup>58</sup> and only slightly slower by Ernst.<sup>62</sup> For a value of  $0.020 (\mu\text{s Torr})^{-1}$  for the deactivation of  $v = 1$ , one obtains a value of  $0.075 (\mu\text{s Torr})^{-1}$  for the V-R,T deactivation rate of  $v = 2$  with the  $v^{1.9}$  scaling. The subtraction of this small contribution from the total rate coefficient of  $0.73 (\mu\text{s Torr})^{-1}$  gives  $0.65 (\mu\text{s Torr})^{-1}$  or  $1.2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the endothermic exchange (13a). If rotational equilibrium is assumed, the exothermic back reaction (-13a) can be calculated to be  $k_{-13a} = 1.9 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 295 K, or with the temperature dependence found by Bott,  $k_{-13a} = 5.6 \times 10^{15} T^{-1} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . We concluded in the previous section that the rate coefficient for the analogous 1,1;0,2 exchange in HF has the slightly smaller rate coefficient of  $4.6 \times 10^{15} T^{-1} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

There are no experimental data for exchanges involving DF( $v > 2$ ) such as



Wilkins' theoretical study<sup>60</sup> found the rate coefficients for exchange (15) to decrease by a factor of 1.6 with each increase in  $v$ , as well as by a factor of  $\exp(-\Delta E_v/RT)$  that results from the endothermicity,  $\Delta E_v$ , of the exchange. An analogy can be made between exchange (15) and exchange (16),





since the latter exchange has endothermicities that increase with  $v$  in the same manner as do the endothermicities of exchange (15). In a study<sup>47</sup> of DF( $v = 1 - 4$ ) relaxation by  $D_2$ , the rate coefficients were found to scale with  $v$  as  $v^{0.5} \exp(-\Delta E_v/RT)$ , where  $\Delta E_v$  is the energy mismatch of the exchange. (The exothermic exchange in the reverse direction scales simply as  $v^{0.5}$ ). Using this analogy and the measured rate coefficient for exchange (13a), we obtain for exchange (15) the rate coefficients,  $k_v = 4 \times 10^{15} v^{0.5} T^{-1} \exp(-\Delta E_v/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The rate coefficients for the exothermic reverse exchange (-15) are simply  $k_v = 4 \times 10^{15} v^{0.5} T^{-1} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

### C. HF (DF) RELAXATION BY DIATOMIC MOLECULES

As mentioned in Section A, several experimental studies of HF( $v$ ) and DF( $v$ ) deactivation by diatomic molecules indicate that the deactivation rates scale as  $v^{2.7 \pm 0.2}$  for HF( $v = 1, 2, 3$ ) and  $v^{1.9 \pm 0.1}$  for DF ( $v = 1 - 4$ ) when the process is exothermic (Reference 47). No evidence of multiquantum processes was found in the studies<sup>63</sup> of HF( $v = 3, 4$ ) deactivation by HF,  $D_2$ ,  $N_2$ . Studies<sup>64, 65</sup> performed at 200 K showed essentially the same  $v$  dependence as that found at 295 K. However, at very high or very low temperatures, the  $v$  dependence could be temperature dependent. For the present review, we will assume single-quantum deactivation processes and the above  $v$  dependences independent of temperature.

#### 1. HF DEACTIVATION

Bott and Cohen<sup>66</sup> measured the deactivation rates for HF(1) in  $H_2$ ,  $D_2$ ,  $N_2$ ,  $O_2$ , DF, HCl, NO, CO, and HBr by the STLIF technique between 295 and about 1000 K. The deactivation process in all of these cases is a combination of V-V and V-R,T processes. No experiments have been performed to determine the exact proportions. However, the data<sup>66</sup> for HF- $H_2$  exchange rates indicate that the deactivation of HF(1) by  $H_2$  occurs chiefly through the V-V exchange process. Fluorescence observed from the infrared-active molecules is also evidence of V-V exchange. Data have been obtained down to 200 to 205 K for HF(1) relaxation in DF by Lucht and Cool<sup>67</sup> and in  $H_2$ ,  $N_2$ , and  $D_2$  by Bott and Heidner.<sup>63</sup> The data<sup>67</sup> for the V-R,T relaxation of DF(1) by HF have essentially the same temperature dependence as data for the V-V and V-R,T relaxa-

tion of HF(1) in DF at temperatures between 200 and 900 K. The theoretical calculations of Poulsen and Billing<sup>61</sup> showed the V-V contribution to the HF(1)-DF rate to be about twice that for the V-R,T contribution at 300 K with the V-R,T contribution dominating at high temperatures. Wilkins,<sup>68</sup> on the other hand, found the V-R,T contribution to be larger than the V-V contribution. For lack of better information, we would recommend  $k(v) = v^{2.7} (1.8 \times 10^{14} T^{-1} + 2.1 \times 10^4 T^{2.26}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for



and  $k(v) = 1.8 \times 10^{14} v^{2.7} T^{-1} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for



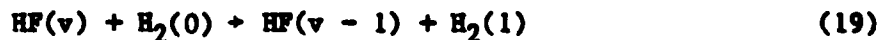
The new measurements<sup>64</sup> for HF( $v = 1, 2, 3$ ) relaxation at 200 K in  $\text{N}_2$  and  $\text{H}_2$  suggest only small changes in the recommended rate coefficients. The relaxation of HF(1) by  $\text{N}_2$  is well-described between 200 and 1500 K by

$$k = (7.4 \times 10^{11} T^{-1} + 14.3 T^3) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

with a  $v^{2.7}$  scaling for the higher vibrational levels. A good fit to the data for the HF(1) V-V exchange with  $\text{H}_2$  between 200 and 1000 K is given by

$$k = 2.4 \times 10^{10} T^{0.5} \exp(167/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

This can be generalized to the V-V exchanges for the higher vibrational levels of HF such as



with the expression

$$k(v) = 2.4 \times 10^{10} v^{0.35} \times T^{0.5} \exp(407 - \Delta E_v)/RT \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

In spite of the  $v^{0.35}$  dependence, this rate coefficient decreases with  $v$  because of its exponential dependence on  $-\Delta E_v/RT$ . The rate coefficient for the reverse exothermic process is simply

$$k(v) = 2.4 \times 10^{10} v^{0.35} \times T^{0.5} \exp(407/RT)$$

Bott<sup>69</sup> has studied the V-R,T relaxation of HF(1) by H<sub>2</sub> from 295 K to 600 K. The data show considerable scatter and only a weak temperature dependence. The scatter in the data results in part from the complications of the V-V vibrational exchange between HF and H<sub>2</sub>. The deactivation of DF(1) by H<sub>2</sub> is not complicated by such V-V exchanges and can be used as a guide to the temperature dependence of the HF(1)-H<sub>2</sub> rate coefficients. The rate coefficients for the DF(1)-H<sub>2</sub> deactivation have been measured at temperatures between 200 and 4000 K<sup>65,69</sup> and can be described by the expression  $k = (1.0 \times 10^{12} T^{-1} + 1.7 \times 10^4 T^{2.28}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  between 200 and 2000 K. The first term in this expression is not precisely determined by the data, and  $T^0$  or  $T^{-2}$  could also be used. However, the similarity of the second term,  $T^{2.28}$ , to the dominant high-temperature dependences of HF and DF self-relaxation should be noted. In absolute value the DF-DF high-temperature term is ~ 30% larger than the DF-H<sub>2</sub> high-temperature term at 1500 K. Attractive forces would be expected to play a much smaller role in DF-H<sub>2</sub> relaxation; this would explain the smaller contribution of the  $T^{-1}$  term at low temperatures. For lack of a better method, at the present time we would recommend using rate coefficients for HF(1)-H<sub>2</sub> and DF(1)-D<sub>2</sub> V-R,T deactivation based on the DF(1)-H<sub>2</sub> rates but scaled to the few measurements of Reference 69. Therefore, for the V-R,T relaxation of HF(v) by H<sub>2</sub>



we would recommend

$$k = v^{2.7} (0.6 \times 10^{12} T^{-1} + 1.0 \times 10^4 T^{2.28}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Such a scaling with  $v$  is consistent with Poole and Smith's interpretation of their data, which are plotted in Fig. 6.

## 2. DF DEACTIVATION

Studies of DF(1) deactivation by HF, D<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, HCl, HBr, NO, DBr, and CO are reviewed in Reference 2. Recent measurements<sup>65</sup> of DF( $v = 1,2,3$ ) relaxation in H<sub>2</sub>, HF, N<sub>2</sub>, and D<sub>2</sub> have been obtained at 200 K as well as at 295 K.<sup>47</sup> New theoretical work includes that of Poulsen and Billing<sup>61</sup> for DF ( $v = 1 - 7$ ) in HF. Our recommended rate coefficient for the V-R,T deactivation of DF( $v$ ) by HF is

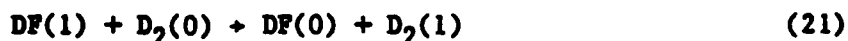
$$k = v^{1.9}(5.2 \times 10^{14} T^{-1.2} + 1.3 \times 10^2 T^3) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

unchanged from the previous recommendation<sup>2</sup> except for the  $v$  scaling.

The rate coefficient that fits the data<sup>2,65</sup> between 200 K and 1000 K for the combined V-V and V-R,T deactivation of DF by N<sub>2</sub> is

$$k = v^{1.9}(1.2 \times 10^{10} + 1.9 \times 10^4 T^2) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The deactivation of DF(1) by D<sub>2</sub> occurs primarily by the energy transfer process



A rate coefficient of  $5.0 \times 10^{11} \exp(-244/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  gives a good fit to the data<sup>70</sup> at temperatures between 295 and 760 K. However, a rate coefficient of

$$k = 1.58 \times 10^{10} \times T^{0.5} \exp(169/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

gives a somewhat better fit to the data between 295 and 760 K and also at 200 K.<sup>65</sup> The rate coefficients for the vibrational exchanges

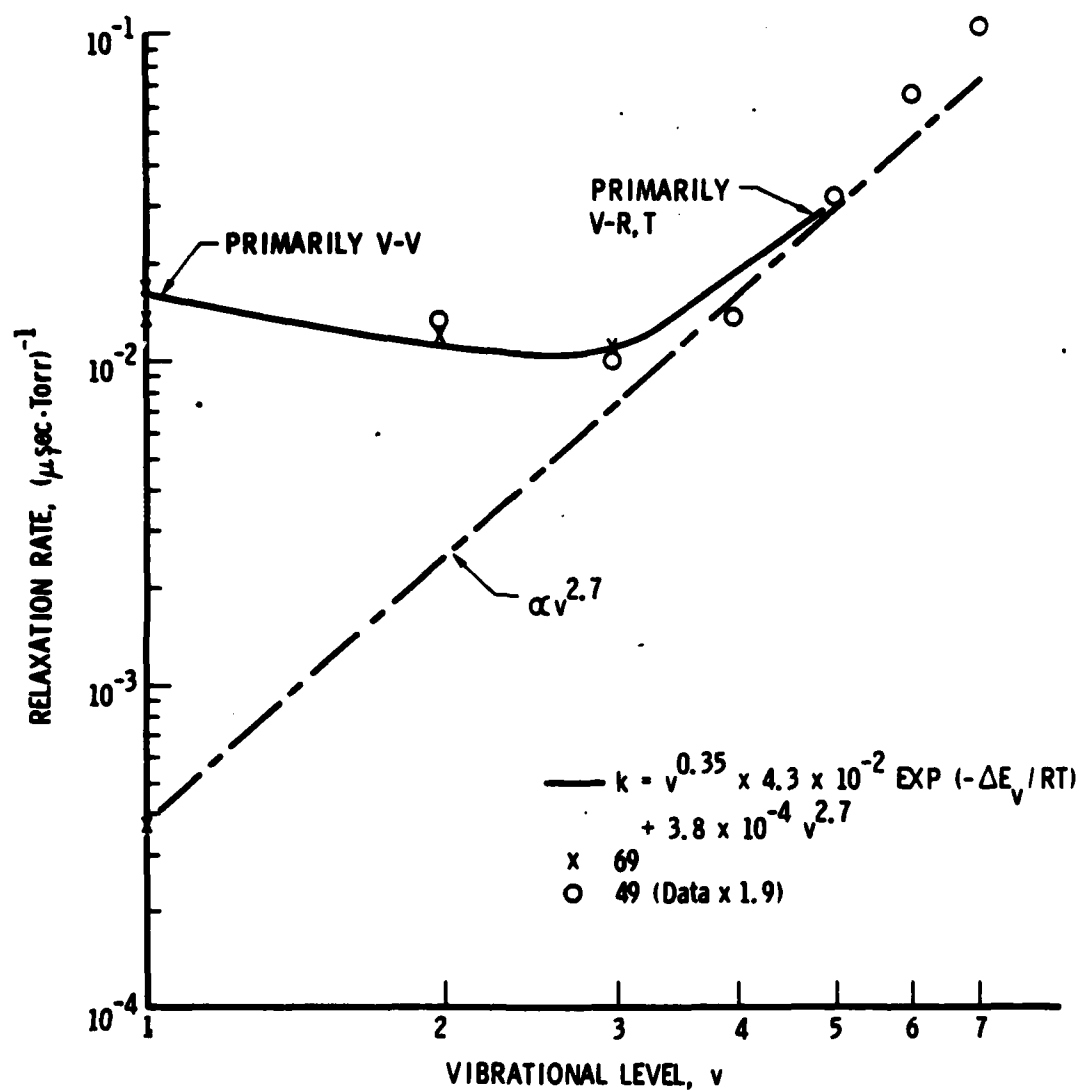
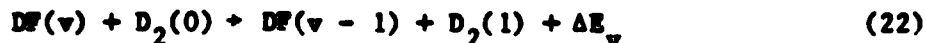


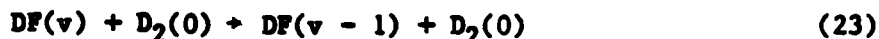
Fig. 6. Relaxation Rates of HF(v) by H<sub>2</sub>. Dashed line is suggested rates for V-R,T process. (T = 295 K).



decrease<sup>48,65</sup> with  $v$  because of the increasing endothermicity of the exchange. The exchange rate coefficients can best be written for the reverse exothermic energy transfer processes:

$$k = 1.58 \times 10^{10} v^{0.5} \times T^{0.5} \exp(407/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Note that this rate coefficient has the same temperature coefficient as that for the analogous  $H_2$ -HF exchange. The V-R,T deactivation process



is much less important. On the basis of the previous discussion for  $HF(v)$ - $H_2$  deactivation, we would recommend  $k = v^{1.9}(1.5 \times 10^{11} T^{-1} + 2.5 \times 10^3 T^{2.28}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

#### D. HF(DF) DEACTIVATION BY ATOMS

##### 1. HF DEACTIVATION BY H ATOMS

The rate coefficients for  $v = 1$  and 2 deactivation are listed in Table 4 and are changed slightly from the previous recommendations,<sup>4</sup> to correct an error in the A factors. In Table 4 the deactivation by H atoms is shown as three separate processes, the first one for all  $v$ , the second for  $v \geq 3$ , and the third for  $v \geq 4$ . For all practical purposes, the first process is important only for  $v = 1$  and 2 because of the large rate coefficients for the second process for  $v \geq 3$ .

Since the last reviews of HF and DF relaxation,<sup>2,4</sup> Bott and Heidner<sup>71</sup> have published their study of  $HF(3)$  deactivation by H and D atoms at 200 K, and Bartoszek et al.<sup>72</sup> have reported their studies of  $HF(v = 1 - 6)$  deactivation by H and D atoms. The results of these two studies show that the rates of  $HF(v = 3 - 6)$  deactivation by H and D atoms are much faster than those of  $HF(v = 1, 2)$ . However, the two studies yield contradictory evidence as to the mechanism of the upper-level deactivation and, therefore, the absolute values of the rate coefficients.

Table 4. Suggested Deactivation Rate Coefficients  
for HF(v) by H Atoms

| $\text{HF}(v) + \text{H} \rightleftharpoons \text{HF}(v') + \text{H}$ $k = A \times 10^{12} \exp(-700/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |                  |     |  |
|---|------------------|-----|--|
| v   | v'               | A   | Reference  |
| 1   | 0                | 0.4 | Haidner and Bott <sup>73</sup>   |
| 2   | 1,0              | 0.7 | Haidner and Bott; <sup>73</sup> with assumption that<br>all possible exit channels are equally<br>probable |
| 3   | 2, 1, 0          |     |  |
| 4   | 3, 2, 1, 0       |     |  |
| 5   | 4, 3, 2, 1, 0    |     |  |
| 6   | 5, 4, 3, 2, 1, 0 |     |  |

| $\text{HF}(v) + \text{H} \rightleftharpoons \text{HF}(v - 1) + \text{H}$ $k = A \times 10^{16} T^{-1} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ |     |  |
|---|-----|--|
| v   | A   | Reference  |
| 3   | 1.4 | Bott and Haidner, <sup>71,74</sup> with assumption<br>of single-quantum deactivation |
| 4   | 2.0 |  |
| 5   | 2.7 |  |
| 6   | 3.5 |  |

| $\text{HF}(v) + \text{H} \rightleftharpoons \text{H}_2(v') + \text{F}$ $k = g_{v,v'} \times 6.0 \times 10^{13} \exp(-500/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |  |           |
|--|--|-----------|
| v  | $g_{v,v'}$                               | Reference |
| 4  | $g_{4,0} = g_{4,1} = 0.5$                | See text  |
| 5  | $g_{5,0} = 0.5, g_{5,1} = 1.0$           |           |
| 6  | $g_{6,0} = g_{6,1} = 0.5, g_{6,2} = 1.5$ |           |

Bott and Heidner made laser-induced fluorescence measurements in a discharge flow-tube apparatus and obtained the rates of HF(3) removal by H and D atoms at 295 K and 200 K. They had previously measured HF( $v = 1, 2, 3$ ) deactivation by H and D atoms at 295 K.<sup>73,74</sup> They obtained a total removal rate of  $(6.3 \pm 1.5) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for HF(3) by H at 295 K and  $(10 \pm 1.2) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 200 K. Channels for HF(3) removal include



and



The kinetic and thermochemical data for the reaction of  $\text{F} + \text{H}_2$  and the known vibrational distribution of product HF can be used to calculate  $k_{25} = (1.4 \pm 0.6) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 295 K if rotational equilibrium is assumed. This is about 22% of the total removal rate measured by Bott and Heidner. Since  $k_{25}$  has a positive activation energy, it should be an even smaller contribution to the total removal rate at 200 K if the initial vibrational distribution produced by the  $\text{F} + \text{H}_2$  does not change drastically. On the basis of these considerations, Bott and Heidner<sup>71</sup> concluded that channel (24) had to be the major deactivation path.

Polanyi and coworkers<sup>72</sup> used the method of chemiluminescence depletion with mass spectrometry (CDMS) to study removal rates of HF( $v = 1 - 6$ ) by D atoms. By this technique they could determine relative depletion rates of the various levels and appearance rates of products. They found the depletion rates of HF( $v$ ) to increase dramatically for  $v = 3$  through 6 from the very low rates for  $v = 1$  and 2. This part of their observation is consistent with the measurements of Bott and Heidner. However, Polanyi and coworkers found only HD to be produced by the removal of HF(3) by D atoms added to HF( $v = 1, 2, 3$ ) formed by the  $\text{F} + \text{CH}_4$  reaction. No HF( $v = 1, 2$ ) increases were observed. These results suggest that the removal of HF(3) by D atoms occurs solely by



the isotopic analog of reaction (25). In other experiments they found the removal of HF(v = 5, 6) correlated with the production of DF. This indicates the exchange process



has a large activation energy of ~ 49 Kcal/mol. An ab initio calculation by Bender et al.<sup>75</sup> indicated that the H-F-H surface has a barrier height of ~ 40 kcal/mol. Preliminary results of a similar calculation by Wadt and Winter<sup>76</sup> also indicate a barrier of  $36 \pm 4$  kcal/mol. These calculated barrier heights are somewhat lower than the ~ 49 kcal/mol indicated by the experiments of Polanyi et al., but are not so small as to be inconsistent.

A mechanism that would account for the fast HF(3) removal rate and the negative activation energy obtained by Bott and Heidner would probably produce HF(2). Polanyi and coworkers did not observe an HF(2) production rate that could be correlated with the HF(3) removal rate. However, they did not compare the relative sensitivities of HD and HF(2) measurements.

Keeping in mind the uncertainty introduced by the work of Polanyi et al. we nevertheless recommend the rate coefficients listed in Table 4 for the deactivation of HF(v = 3 - 6) by H atoms. The  $T^{-1}$  temperature dependence fits the measurements of Bott and Heidner at 200 and 295 K and makes this deactivation mechanism of less importance at higher temperatures. The A factor has been calculated by subtracting the contribution of reaction (25) from the measured removal rate. The A factors have been chosen to increase with v.

The removal rates of HF(v > 3) by H atoms by the reaction



have been reported by Wilkins,<sup>77</sup> who performed Monte Carlo trajectory calculations. He found the A factors to increase somewhat with v. Based on the recommended value of the F + H<sub>2</sub> rate coefficient, the distribution over vibrational levels, and the JANAF equilibrium constant, the rate coefficient for

reaction (27) for  $v = 3$  is  $k = 1.8 \times 10^{13} T^{0.179} \exp(-760/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  near 295 K. Using Wilkins' calculations as a guide to the activation energy and distributions over  $v'$ , we would suggest

$$k_{27}(v, v') = g_{v, v'} \times 6.0 \times 10^{13} \exp(-500/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

with  $g_{4,0} = g_{4,1} = 0.5$ ;  $g_{5,0} = 0.5$ ,  $g_{5,1} = 1$ ; and  $g_{6,0} = g_{6,1} = 0.5$ ,  $g_{6,2} = 1.5$ . These rate coefficients are somewhat larger than those previously recommended,<sup>1</sup> but are smaller than the present recommendation for the deactivation processes (24).

## 2. DF DEACTIVATION BY D ATOMS

Experimental data for DF( $v$ ) deactivation by D atoms are almost non-existent. Heidner and Bott<sup>73</sup> studied the deactivation of HF(1) and DF(1) by H and D atoms and obtained a relaxation rate coefficient of  $(0 \pm 9) \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the deactivation process



compared to  $(1.4 \pm 0.4) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the deactivation rate of HF(1) by H. In the same paper they found D atoms to be only 1/10 as effective as H atoms in the deactivation of HF(1), and H atoms to be twice as effective on HF(1) as on DF(1). This raises the possibility of the relaxation rate of (28) being ~1/10 to ~1/20 of that for  $\text{H} + \text{HF}(1)$ , or  $1 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Such a low value would mean that deactivation of DF( $v < 4$ ) by D atoms is probably not significant for chemical laser modeling. Wilkins<sup>77</sup> performed trajectory calculations and found for  $v = 1$  that  $k_{\text{H} + \text{HF}}/k_{\text{D} + \text{DF}} = 3.8$  at room temperature with  $k_{\text{D} + \text{DF}} = 10^{13} \exp(-2000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . If we take his activation energy and scale down the A factor so that  $k = 4 \times 10^{11} \exp(-2000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , we obtain  $1.3 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 295 K. This A factor is the same as that for the  $\text{H} + \text{HF}(1)$  deactivation rate coefficient. For lack of better information we will assume the rate coefficient to be the same for the various  $v, v'$  processes.

As in the case of HF, the deactivation of levels of  $v > 5$  by the reactions



can be scaled from the rate coefficient for  $v = 4$ . Using the recommended rate coefficient for  $F + D_2$ , the distribution over  $v$ , and the equilibrium constant, we calculate  $k_{29}(4,0) = 3.3 \times 10^{11} T^{0.59} \exp(17/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $v = 4$  and  $v' = 0$ . This has a value of  $1.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $T = 295 \text{ K}$ . For  $v > 5$  we will assume  $k_{29}(v, v') = v \times 10^{13} [\exp(-500/RT)]/(v-3) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  with the rate being equally probable for all values of  $v'$  for which the reaction is exothermic. This distribution over  $v'$  differs from that recommended for  $H + HF(v)$ , for which more calculations are available. There are no experimental data in either case.

There may be a deactivation process for  $DF(v > 4)$  analogous to that proposed for  $HF (v > 3)$  with the  $1/T$  temperature dependence. For the present it does not seem warranted to speculate on what rate coefficients such a process might have. Since  $D + DF(1)$  is much less efficient than  $H + HF(1)$ , the  $D + DF(4)$  deactivation rate coefficient may be correspondingly slower, and therefore small with respect to the removal rate of  $DF(4)$  in reaction (29).

### 3. HF AND DF DEACTIVATION BY F ATOMS

Experimental and theoretical studies have been reviewed in Reference 2. A rate coefficient of  $k = 4 \times 10^{13} \exp(-2700/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the deactivation of  $DF(1)$  by  $F$  is in substantial agreement with the room-temperature measurements and the theoretical activation energy.<sup>2</sup> Also, we recommend  $k = 1.7 \times 10^{13} \exp(-2700/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $HF(1)$  deactivation by  $F$ . These rate coefficients disagree somewhat with high-temperature ( $\sim 2000 \text{ K}$ ) data, but should hold at the lower temperatures at which chemical lasers operate. For lack of better information, we have assumed single quantum deactivation and the same  $v^n$  scaling that holds for deactivation by diatomic molecules. The theoretical calculations (see Ref. 2) predicted faster rate coefficients, multiquantum relaxation, and a somewhat slower scaling with  $v$ .

#### 4. HF AND DF DEACTIVATION BY Ar AND He

Within the accuracy of the experimental data,<sup>78</sup> the relaxation times of DF(1) and HF(1) in Ar appear to have very similar temperature dependences, with HF(1) being relaxed 1.3 to 1.5 times as fast as DF between 1500 and 4000 K. The HF(1) and DF(1) relaxation times in helium also have similar temperature dependences,<sup>78</sup> with the HF(1)-He rate being faster than the DF(1)-He rate by a factor of  $\approx 1.3$ . For deactivation by Ar, we previously recommended  $k = A \times 10^{-5} T^{4.3} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , with  $A = 7$  for DF(1) and  $A = 9$  for HF(1). For deactivation by He, we had recommended  $k = A \times 10^{-5} T^{4.75} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , with  $A = 0.4$  for DF(1) and  $A = 0.6$  for HF(1). Not a great deal of error is introduced by using a  $T^{4.5}$  temperature dependence for both He and Ar and setting  $A = 1.6$  and  $2.5$  for the deactivation of DF by Ar and He, respectively, and  $A = 2.0$  and  $3.7$  for the deactivation of HF by Ar and He, respectively.

#### E. HF AND DF RELAXATION BY POLYATOMIC MOLECULES

Because of the interest in the DF-CO<sub>2</sub> transfer laser, HF and DF relaxation in CO<sub>2</sub> has been studied in depth. The DF-CO<sub>2</sub> kinetics have been discussed in Reference 2, and those recommendations remain in effect. New studies of the  $v$  dependence for the HF( $v$ )-CO<sub>2</sub> and DF( $v$ )-CO<sub>2</sub> deactivation rates have been reported in References 49, 56, and 79, and 47, 49, and 79, respectively. The rate coefficients were found to increase with  $v$  approximately as  $v^2$  at 295 K.

The vibrational relaxation of HF(1) and DF(1) in the presence of a number of other polyatomic molecules has been studied mostly at room temperature. We have collected most of these data in Table 5. HF vibrational relaxation rates have been correlated<sup>80</sup> with the energy mismatch between the HF fundamental frequency and the vibrational frequency of the polyatomic molecules (usually a strong, fundamental, infrared-active one). The correlations are reasonably good (within a factor of 3 deviation from linearity), indicating that the principal mode of deactivation is, in all probability, V-V transfer rather than just V-R,T transfer. A simple correlation for DF relaxation rates is shown in Fig. 8 of Reference 2. The relaxation rate coefficients are plotted

Table 5. Comparison of HF(v = 1) and DF(v = 1) Deactivation by Polyatomic Molecules at Room Temperature

| Deactivating Molecule                        | HF(v = 1)<br>k, ( $\mu$ s Torr) <sup>-1</sup> | Ref. | DF(v = 1)<br>k, ( $\mu$ s Torr) <sup>-1</sup> | Ref. |
|--|---|------|---|------|
| CH <sub>4</sub>                              | 5.3 × 10 <sup>-2</sup>                        | 81   | (2.2 ± 0.1) × 10 <sup>-1</sup>                | 83   |
|  | 6.4 × 10 <sup>-2</sup>                        | 82   |   |      |
|  | 2.1 × 10 <sup>-2</sup>                        | 80   |   |      |
|  | (2.6 ± 0.3) × 10 <sup>-2</sup>                | 83   |   |      |
|  | 3.5 × 10 <sup>-2</sup>                        | 84   |   |      |
| CH <sub>3</sub> F                            |   |      | (0.36 ± 0.04)                                 | 83   |
| CH <sub>2</sub> H <sub>6</sub>               | 11 × 10 <sup>-2</sup>                         | 81   | (6.1 ± 1.0) × 10 <sup>-1</sup>                | 83   |
|  | 5.6 × 10 <sup>-2</sup>                        | 82   |   |      |
|  | (5.9 ± 0.6) × 10 <sup>-2</sup>                | 83   |   |      |
|  | 9.3 × 10 <sup>-2</sup>                        | 84   |   |      |
| C <sub>3</sub> H <sub>8</sub>                | 13.5 × 10 <sup>-2</sup>                       | 81   |   |      |
|  | 8.3 × 10 <sup>-2</sup>                        | 82   |   |      |
|  | (8.4 ± 0.9) × 10 <sup>-2</sup>                | 83   |   |      |
| C <sub>4</sub> H <sub>10</sub>               | 17 × 10 <sup>-2</sup>                         | 84   | (12.6 ± 1.5) × 10 <sup>-1</sup>               | 83   |
|  | (12.8 ± 0.9) × 10 <sup>-2</sup>               | 83   |   |      |
| C <sub>2</sub> H <sub>2</sub>                | 5.9 × 10 <sup>-2</sup>                        | 82   | (4.0 ± 0.6) × 10 <sup>-2</sup>                | 83   |
|  | 3 × 10 <sup>-1</sup>                          | 85   | (2.34 ± 0.03) × 10 <sup>-1</sup>              | 87   |
| C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> | (2.7-3.1) × 10 <sup>-2</sup>                  | 84   | (1.86 ± 0.2) × 10 <sup>-2</sup>               | 83   |
| C <sub>2</sub> H <sub>4</sub>                | ~ 5 × 10 <sup>-2</sup>                        | 82   | (1.75 ± 0.2) × 10 <sup>-1</sup>               | 83   |
|  | 4.9 × 10 <sup>-2</sup>                        | 84   |   |      |
| C <sub>6</sub> H <sub>6</sub>                | 3.6 × 10 <sup>-1</sup>                        | 85   | (3.9 ± 0.02) × 10 <sup>-1</sup>               | 87   |
| CS <sub>2</sub>                              | 1.6 × 10 <sup>-2</sup>                        | 85   | (4.6 ± 0.07) × 10 <sup>-2</sup>               | 87   |
| COF <sub>2</sub>                             | (5.74 ± 0.5) × 10 <sup>-2</sup>               | 86   | (3.81 ± 0.05) × 10 <sup>-2</sup>              | 87   |
| SO <sub>2</sub>                              | (2.4 ± 0.3) × 10 <sup>-2</sup>                | 86   | (1.27 ± 0.15) × 10 <sup>-2</sup>              | 83   |
| BF <sub>3</sub>                              | (1.53 ± 0.15) × 10 <sup>-3</sup>              | 86   | (7.0 ± 1.0) × 10 <sup>-3</sup>                | 83   |
| CF <sub>4</sub>                              | < (4.2 ± 0.6) × 10 <sup>-4</sup>              | 86   | < (1.0 ± 0.1) × 10 <sup>-3</sup>              | 83   |
|  | < (4.2 ± 0.6) × 10 <sup>-4</sup>              | 80   | 1.1 × 10 <sup>-3</sup>                        | 83   |
| CBrF <sub>3</sub>                            | < (3.9 ± 0.6) × 10 <sup>-4</sup>              | 86   | < (5.8 ± 0.6) × 10 <sup>-4</sup>              | 85   |
| CF <sub>3</sub> H                            |   |      | (1.95 ± 0.25) × 10 <sup>-2</sup>              | 83   |

Table 5. Comparison of HF(v = 1) and DF(v = 1) Deactivation  
by Polyatomic Molecules at Room Temperature (Continued)

| Deactivating<br>Molecule        | HF(v = 1)<br>k, ( $\mu$ s Torr) <sup>-1</sup> | Ref. | DF(v = 1)<br>k, ( $\mu$ s Torr) <sup>-1</sup> | Ref. |
|---------------------------------|---|------|---|------|
| NF <sub>3</sub>                 | < 3 × 10 <sup>-4</sup>                        | 86   | < 5 × 10 <sup>-4</sup>                        | 83   |
|                                 | < 3 × 10 <sup>-4</sup>                        | 85   | 4.9 × 10 <sup>-4</sup>                        | 85   |
| SF <sub>6</sub>                 | < 5 × 10 <sup>-5</sup>                        | 86   | (2.58 ± 0.05) × 10 <sup>-4</sup>              | 87   |
| H <sub>2</sub> O                | (4.1 ± 0.5)                                   | 88   |   |      |
| D <sub>2</sub> O                | (4.1 ± 0.5)                                   | 88   |   |      |
| H <sub>2</sub> S                | 7.8 × 10 <sup>-2</sup>                        | 80   |   |      |
|                                 | (6.1 ± 0.7) × 10 <sup>-2</sup>                | 86   |   |      |
| SiF <sub>4</sub>                | (3.5 ± 0.3) × 10 <sup>-4</sup>                | 86   |   |      |
| C <sub>2</sub> HF <sub>3</sub>  | 1.9 × 10 <sup>-2</sup>                        | 84   |   |      |
| C <sub>2</sub> H <sub>3</sub> F | 3.4 × 10 <sup>-2</sup>                        | 84   |   |      |
| C <sub>2</sub> F <sub>4</sub>   | 3.5 × 10 <sup>-3</sup>                        | 84   |   |      |
| C <sub>2</sub> F <sub>6</sub>   | (1.6 ± 0.4) × 10 <sup>-4</sup>                | 86   |   |      |
| C <sub>4</sub> F <sub>8</sub>   | (6.3 ± 0.4) × 10 <sup>-4</sup>                | 86   |   |      |
| PF <sub>5</sub>                 | (7.3 ± 0.6) × 10 <sup>-3</sup>                | 86   |   |      |
| SO <sub>2</sub> F <sub>2</sub>  | (1.41 ± 0.15) × 10 <sup>-2</sup>              | 86   |   |      |
| N <sub>2</sub> O                | (3.4 ± 0.3) × 10 <sup>-2</sup>                | 86   |   |      |
|                                 | 1.2 × 10 <sup>-2</sup>                        | 80   |   |      |
| HCN                             | (1.72 ± 0.4) × 10 <sup>-1</sup>               | 89   | (1.07 ± 0.14) × 10 <sup>-1</sup>              | 89   |

based on the closest-to-resonant vibrational mode of the polyatomic molecule. There is considerable scatter, but the graph does show a strong dependence of  $k$  on  $\Delta E$ .

There have been few studies of the temperature dependence of these deactivation rates. The DF(1)-CO<sub>2</sub> rate coefficient has an inverse temperature dependence below about 600 K (Fig. 6 of Reference 2); a similar minimum at about 600 K occurs in the data<sup>66</sup> for HF(1)-CO<sub>2</sub>. Bott<sup>83</sup> found the rate coefficient for DF(1)-CH<sub>4</sub> deactivation to decrease with increasing temperature (approximately as  $T^{-0.5}$ ) between 295 K and 750 K when expressed in units of cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. The rate coefficient for DF(1)-CF<sub>4</sub> was found<sup>83</sup> to be insensitive to temperature in this temperature range. McGarvey et al.<sup>89</sup> found the rate coefficients for HF(1) and DF(1) deactivation by HCN to vary with temperature as  $T^{-1}$  around 295 K. As a general rule, it appears that the faster the rate coefficient, the more likely it is to have an inverse temperature dependence around room temperature. Attractive forces may account for the faster rate coefficients and their inverse temperature dependence. In those collisions for which the attractive forces are less important than the short-range forces, the rate coefficients are more likely to increase with temperature.

Besides the previously mentioned studies of the deactivation of HF( $v$ ) and DF( $v$ ) by CO<sub>2</sub>, little is known about the deactivation rates of the upper vibrational levels. Kwok and Cohen<sup>80</sup> measured rates for HF( $v = 1, 2, 3$ ) deactivation by H<sub>2</sub>S, CH<sub>4</sub>, and CF<sub>4</sub> and found the rate coefficients to scale somewhat faster than  $v$ . Lambert et al.<sup>55</sup> measured deactivation rates for HF( $v = 3, 4$ ) in CH<sub>4</sub> and CD<sub>4</sub> and found the rates for  $v = 4$  to be  $\sim 2.8$  times the rate for  $v = 3$ . Arnold and Kimball<sup>84</sup> studied the deactivation of HF( $v = 1, 2$ ) by several fluoroethylenes and found the  $v = 2$  rates to be faster than those for  $v = 1$  by factors between 1.9 to 2.7. If these data and the CO<sub>2</sub> data are typical, a  $v$  scaling between  $v$  and  $v^2$  would be a good estimate where no other data are available.

#### F. VIBRATIONAL RELAXATION OF H<sub>2</sub> AND D<sub>2</sub>

The recommended gas-phase relaxation rates of H<sub>2</sub> and D<sub>2</sub> are unchanged from previous reviews.<sup>1,2</sup> Heterogeneous relaxation of vibrationally excited

hydrogen molecules has been investigated by Heidner and Kasper<sup>90</sup> and Orkin et al.<sup>91</sup> and found to depend on surface condition as well as surface material. Such deactivation processes would probably be of consequence only downstream of any laser cavity.



## V. ROTATIONAL RELAXATION

Initial attempts to model HF chemical laser performance were based on the assumption of infinitely fast rotational relaxation rates with a consequent Boltzmann distribution over the various rotational levels.<sup>92</sup> The computer codes such as RESALE give reasonable agreement with experimental measurements of total power or energy but do not predict spectral output or line sequencing.<sup>93</sup> More sophisticated codes have been used to predict the effects of finite rotational relaxation rates on total power and spectral output.<sup>94-100</sup>

There are several different approaches to the inclusion of rotational relaxation processes. A code can be constructed with detailed reaction kinetics for each vibrational-rotational state interacting with every other vibrational-rotational state. Such a complicated code will have long running times and will require detailed rate coefficients. For more approximate calculations a code can use rotational relaxation times instead of detailed rotational kinetics to describe the relaxation toward a Boltzmann distribution.

The difficulties of pumping a single state, monitoring the population of that state, and determining the product channels have hindered experimental studies. The most extensive series of studies has been performed by Hinch and Hobbs.<sup>101-103</sup> In a study of the rotational relaxation of HF( $v = 0, J$ ) in HF-HF collisions at 295 K, they<sup>102</sup> used a pulsed laser to deplete a specific  $J$  level and monitored the population of that level with a continuous-wave laser tuned to the same frequency as the pump laser. The depleted levels were found to fill at rates shown in Fig. 7. Peterson et al.<sup>104</sup> used a pulsed laser to deplete a  $v = 0$  vibrational-rotational level of HF and then used the tail of the same laser pulse attenuated with a Kerr cell to monitor the filling of the level. Their results are in close agreement with those of Hinch and Hobbs. Gur'ev et al.<sup>105</sup> performed bleaching experiments in which the energies absorbed in a cell containing HF at various pressures and laser power densities were measured and used to deduce the rotational relaxation rates. Their deduced rate for  $J = 8$  is about 10 times lower than that of Hinch. In all three of these studies, only the total filling rate of a chosen  $J$  level was

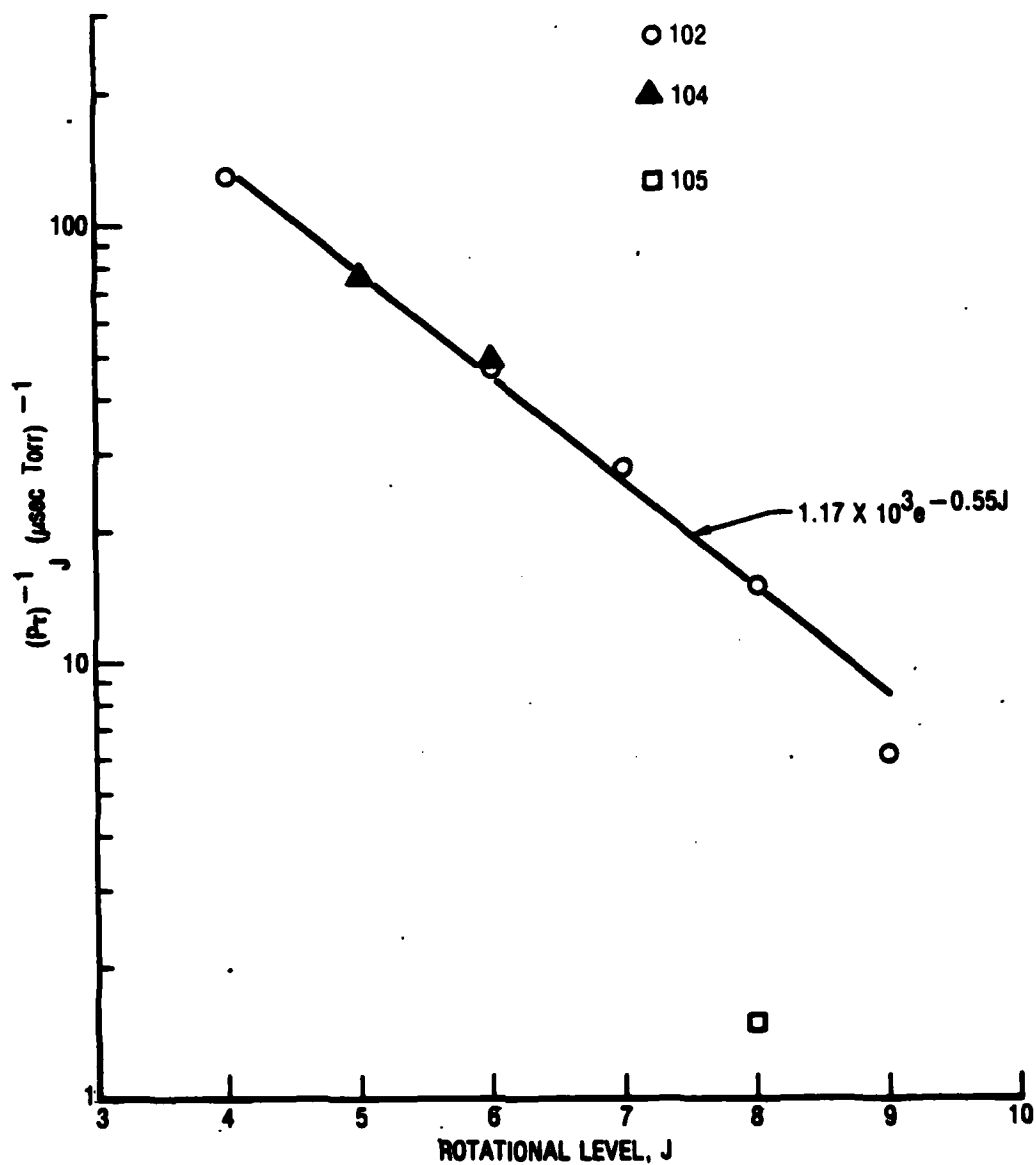


Fig. 7. Rotational Relaxation Rates Determined from Depletion and Refilling Rate Measurements for HF(v,J)

measured, and the filling processes may include multiquantum processes as well as single-quantum processes. One problem that might affect the interpretation of these experiments is line-burning of the spectral profile and subsequent redistribution of velocities in that vibrational-rotational level. However, preliminary results of Hinchey and Hobbs<sup>101</sup> were interpreted to indicate that the velocity redistribution occurs on a slower time scale, at least for  $J = 3$ .

Other rotational relaxation data include the detailed measurements by Hinchey<sup>101</sup> of the rise times of various rotational levels in  $v = 1$  after the fast pumping of specific rotational level in  $v = 1$  by an HF-pulsed laser. Lang, Polanyi, and Wanner<sup>106</sup> measured with a laser infrared fluorescence technique the relative rotational relaxation rates for HF( $v = 1, J = 3, 5$ ) in collisions with argon. These are the only experimental data for product channels of rotational relaxation. Both of these studies differ from the studies of  $v = 0$  in a basic way. In the  $v = 0$  studies, the populations of all rotational levels are characterized by a Boltzmann distribution except the one being perturbed. In the  $v = 1$  studies, there is essentially no population in  $v = 1$  except the initially pumped rotational level, and all rotational levels have to relax toward a Boltzmann distribution. Care has to be taken in comparing directly the results for  $v = 1$  and  $v = 0$ .

A rotational relaxation model has to be assumed in order to interpret and generalize the observed data. Lang, Polanyi, and Wanner<sup>106</sup> fitted their data for HF(1,J)-Ar with an R-T model with rotational energy being converted into translational energy. Such a model may not be appropriate for HF-HF collisions where R-R processes may play a role. Hinchey and Hobbs<sup>101-103</sup> used an R-R, T model to fit their data for HF-HF rotational relaxation while Sentman<sup>107</sup> fitted the same data with the Polanyi-Woodall R-T model.<sup>108</sup> The description of the data also depends on its use. For instance, only exponential decay times for each vibrational rotational level are required for Rough's code.<sup>99</sup>

Hinchey and Hobbs<sup>101</sup> found  $H_2$  and He to be less effective relaxers than HF itself by factors of 10 and 30, respectively. Gur'ev et al.<sup>105</sup> performed bleaching experiments of HF(0,  $J = 8$ ) in the presence of HF,  $H_2$ ,  $D_2$ , He, Ar, Xe,  $O_2$ ,  $F_2$ , CO,  $CO_2$ ,  $CS_2$ , and  $CCl_4$ ; they found  $H_2$  to be less effective than HF by a factor of 30, the rare gases less effective by at least a factor of 200.

Theoretical studies of rotational relaxation of HF have been reported by DePristo and Alexander,<sup>109</sup> Wilkins,<sup>110</sup> and Feldmann and Ben-Shaul.<sup>111</sup> A detailed review of these will not be presented. However, DePristo and Alexander, and Wilkins reported that their calculated values were much smaller than the data of Hinch and Hobbs would indicate. Pritchard and coworkers<sup>112</sup> have recently proposed the expression

$$\sigma_{J \rightarrow J'} = (2J' + 1) (T_f/T_i)^{1/2} (\Delta E_{JJ'})^{-\lambda}$$

for the R  $\rightarrow$  T cross sections  $\sigma_{J \rightarrow J'}$ , where  $T_i$  and  $T_f$  are the initial and final relative translational energies, and  $(\Delta E_{JJ'})^{-\lambda}$  is the energy difference between the states raised to some power  $-\lambda$ . Experiments performed by Polanyi and coworkers<sup>113</sup> for HF + Ar were in good agreement with the above expression.

In summary, specific recommendations for rate coefficients or even rotational relaxation processes are beyond the intent of the present review. As pointed out by Sentman,<sup>100</sup> even though rotational relaxation processes are apparently very fast relative to other chemical reactions, the rates of deactivation by laser action are frequently of the same order of magnitude. Therefore, the rotational relaxation rates as well as the initial vibrational-rotational distributions are important in determining the spectral power distributions. Figure 1 of Reference 100 shows the similarity of the spectral distribution using rate coefficients that Sentman obtained<sup>107</sup> by fitting them to the data of Hinch and Hobbs. The distribution is in reasonable agreement with the experimental data and would lend support to the fast rotational relaxation rates.

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# APPENDIX A. RECOMMENDED RATE COEFFICIENTS FOR H<sub>2</sub>-F<sub>2</sub> SYSTEM

| Reaction Number | Reaction  | Rate Coefficient,<br>Units of cm. mole, sec, cal   | M, v, A, g(v)  |
|-----------------|---|--|--|
| 1a              | 2H + M <sub>1</sub> ⇌ H <sub>2</sub> (g) + M <sub>1</sub>                   | k <sub>1</sub> <sup>H</sup> = 6.2 × 10 <sup>17</sup> T <sup>-0.95</sup>  | M = all species except H and H <sub>2</sub>  |
| 1b              | 2H + H <sub>2</sub> ⇌ H <sub>2</sub> (g) + H <sub>2</sub>                   | k <sub>1</sub> <sup>H<sub>2</sub></sup> = 9.4 × 10 <sup>16</sup> T <sup>-0.61</sup>  |  |
| 1c              | 2H + H ⇌ H <sub>2</sub> (g) + H   | k <sub>1</sub> <sup>H</sup> = 1.2 × 10 <sup>14</sup> T <sup>0.5</sup>  |  |
| 2               | F <sub>2</sub> + H <sub>2</sub> ⇌ 2F + H <sub>2</sub>                       | k <sub>2</sub> <sup>H</sup> = 5 × 10 <sup>13</sup> A <sub>H</sub> exp(-35,100/RT)  | A <sub>F</sub> = 10, A <sub>F<sub>2</sub></sub> = 2.7, A <sub>He</sub> = 2;<br>A <sub>M</sub> = 1, all other M   |
| 3               | HF(v) + H <sub>3</sub> ⇌ H + F + H <sub>3</sub>                             | k <sub>3,v</sub> = $\frac{1.2 A_H}{n+1} \times 10^{19} T^{-1}$<br>$\exp[(-135,100 + E_v - E_0)/RT]$  | A <sub>F</sub> = A <sub>H</sub> = A <sub>HF</sub> = 5; A <sub>M</sub> = 1, all other M;<br>v = 0...n   |
| 4a              | F + H <sub>2</sub> (g) ⇌ HF(v) + H  | k <sub>4,v</sub> = g(v) × 2.6 × 10 <sup>12</sup> T <sup>0.5</sup> exp(-610/RT)   | v = 1,2,3; g(1) = 0.15, g(2) = 0.55,<br>g(3) = 0.30  |
| 4b              | HF(v) + H ⇌ H <sub>2</sub> (v') + F   | k <sub>4b(v,v')</sub> = g <sub>v</sub> (v') × 6.0 × 10 <sup>13</sup> exp(-500/RT)  | g <sub>4</sub> (0) = g <sub>4</sub> (1) = 0.5; g <sub>5</sub> (0) = 0.5,<br>g <sub>5</sub> (1) = 1.0; g <sub>6</sub> (0) = g <sub>6</sub> (1) = 0.5,<br>g <sub>6</sub> (2) = 1.5 |
| 5               | H + F <sub>2</sub> ⇌ HF(v) + F  | k <sub>5,v</sub> = g(v) × 3.0 × 10 <sup>9</sup> T <sup>1.5</sup> exp(-1680/RT)   | g(v < 2) = 0; g(3) = 0.07, g(4) = 0.13,<br>g(5) = 0.23, g(6) = 0.33, g(7) = 0.15,<br>g(8) = 0.12   |
| 6a              | HF(v) + HF ⇌ HF(v-1) + HF   | k <sub>6a,v</sub> <sup>HF</sup> = v <sup>2.6</sup> (3 × 10 <sup>14</sup> T <sup>-1</sup> + 3.5 × 10 <sup>4</sup> T <sup>2.26</sup> )   | v = 1...6  |
| 6b              | HF(v) + H <sub>2</sub> ⇌ HF(v-1) + H <sub>2</sub>                           | k <sub>6b,v</sub> <sup>H<sub>2</sub></sup> = v <sup>2.7</sup> (6 × 10 <sup>11</sup> T <sup>-1</sup> + 1.0 × 10 <sup>4</sup> T <sup>2.28</sup> )  | v = 1...6  |
| 6c              | HF(v) + H <sub>4</sub> ⇌ HF(v-1) + H <sub>4</sub>                           | k <sub>6c,v</sub> <sup>H<sub>4</sub></sup> = A <sub>H</sub> × 10 <sup>-5</sup> v <sup>2.7</sup> T <sup>4.5</sup>   | A <sub>Ar</sub> = A <sub>F<sub>2</sub></sub> = 2; A <sub>He</sub> = 3.7  |
| 6d              | HF(v) + H ⇌ HF(v') + H  | k <sub>6d(v,v')</sub> <sup>H</sup> = g(v,v') × 10 <sup>12</sup> exp(-700/RT)   | g(1,0) = 0.4; g(v,v') = 0.7 for v > 2 and<br>v' < v  |
| 6e              | HF(v) + H ⇌ HF(v-1) + H   | k <sub>6e,v</sub> <sup>H</sup> = g(v) × 10 <sup>16</sup> T <sup>-1</sup>   | g(3) = 1.4; g(4) = 2.0; g(5) = 2.7;<br>g(6) = 3.5  |
| 6f              | HF(v) + F ⇌ HF(v-1) + F   | k <sub>6f,v</sub> <sup>F</sup> = 1.9 × 10 <sup>13</sup> v <sup>2.7</sup> exp(-2700/RT)   | v = 1...6  |
| 6g              | HF(v) + DF ⇌ HF(v-1) + DF   | k <sub>6g,v</sub> <sup>DF</sup> = v <sup>2.7</sup> (1.8 × 10 <sup>14</sup> T <sup>-1</sup> + 2.1 × 10 <sup>4</sup> T <sup>2.26</sup> )   | v = 1...6  |
| 7               | HF(v) + DF(g) ⇌ HF(v-1) + DF(l)   | k <sub>7,v</sub> = v <sup>2.7</sup> × 1.8 × 10 <sup>14</sup> T <sup>-1</sup>   | v = 1...6  |
| 8               | HF(v) + HF(v') ⇌ HF(v+1) + HF(v'-1)   | k <sub>8(v,1;v+1,0)</sub> = (v+1) <sup>0.35</sup> × 3.6 × 10 <sup>15</sup> T <sup>-1</sup><br>k <sub>8(v,v';v+1,v'-1)</sub> = (v+1) <sup>0.35</sup> × 2.8 × 10 <sup>15</sup> T <sup>-1</sup> | v = 1...6; v' = 1<br>v = 2...6; v > v' > 2   |
| 9               | HF(v-1) + H <sub>2</sub> (l) ⇌ HF(v) + H <sub>2</sub> (g)                   | k <sub>9,v</sub> = v <sup>0.35</sup> × 2.4 × 10 <sup>10</sup> × T <sup>0.5</sup> exp(407/RT)   | v = 1...6  |
| 10              | HF(v) + H <sub>2</sub> (g) ⇌ HF(v-1) + H <sub>2</sub> (l)                   | k <sub>10,v</sub> = v <sup>2.7</sup> (7.4 × 10 <sup>11</sup> T <sup>-1</sup> + 14.3 T <sup>3</sup> )   | v = 1...6  |
| 11a             | H <sub>2</sub> (v) + H <sub>5</sub> ⇌ H <sub>2</sub> (v-1) + H <sub>5</sub> | k <sub>11a,v</sub> <sup>H<sub>5</sub></sup> = v × 2.5 × 10 <sup>-4</sup> T <sup>4.3</sup> A <sub>H<sub>5</sub></sub>   | A <sub>H<sub>2</sub></sub> = 4, A <sub>Ar</sub> = 1; v > 1   |
| 11b             | H <sub>2</sub> (v) + H ⇌ H <sub>2</sub> (v-1) + H                           | k <sub>11b,v</sub> <sup>H</sup> = 2 × 10 <sup>13</sup> exp(-2720/RT)   | v > 1  |

# APPENDIX B. RECOMMENDED RATE COEFFICIENTS FOR D<sub>2</sub>-F<sub>2</sub> SYSTEM

| Reaction Number | Reaction   | Rate Coefficient,<br>Units of cm, mole, sec, cal  | M, v, A, g(v)   |
|-----------------|--|---|---|
| 1a              | 2D + Ar $\rightleftharpoons$ D <sub>2</sub> + Ar                                 | $k_{1Ar} = 10^{18} T^{-1}$  | Use $k_{1Ar}$ for all M other than D, D <sub>2</sub>  |
| 1b              | 2D + D <sub>2</sub> $\rightleftharpoons$ D <sub>2</sub> + D <sub>2</sub>         | $k_{1D_2} = 10^{17} T^{-0.67}$  |   |
| 1c              | 2D + D $\rightleftharpoons$ D <sub>2</sub> + D                                   | $k_{1D}^D = 3 \times 10^{17} T^{-0.5}$  |   |
| 2               | F <sub>2</sub> + M $\rightleftharpoons$ 2F + M                                   | $k_2^M = 5 \times 10^{13} A_M \exp(-35,100/RT)$   | $A_F = 10, A_{F_2} = 2.7, A_{He} = 2;$<br>$A_M = 1, \text{ all other M}$  |
| 3               | DF(v) + M $\rightleftharpoons$ D + F + M   | $k_{3,v}^M = \frac{2.7 A_M}{n+1} \times 10^{22} T^{-2} \times$<br>$\exp[(-137,130 + E_v - E_0)/RT]$ | $A_D = A_F = A_{DF} = 5; A_M = 1 \text{ for}$<br>all others; $v = 0 \dots n$  |
| 4a              | F + D <sub>2</sub> (v) $\rightleftharpoons$ DF(v) + D                            | $k_{4,v} = g(v) \times 2.0 \times 10^{12} T^{n(v)} \exp(-830/RT)$                                   | $v = 1 \dots 4; g(1) = 0.07, g(2) = 0.23,$<br>$g(3) = 0.46, g(4) = 0.28; n(1) =$<br>$n(2) = 0.5; n(3) = n(4) = 0.49$                                    |
| 4b              | DF(v) + D $\rightleftharpoons$ F + D <sub>2</sub> (v')                           | $k_{4,v,v'} = 10^{13} \exp(-500/RT) \times v/(v-3)$   | $v' \leq v-4; v = 5 \dots 13.$  |
| 5               | D + F <sub>2</sub> $\rightleftharpoons$ DF(v) + F                                | $k_{5,v} = g(v) \times 2.0 \times 10^9 T^{1.5} \exp(-1650/RT)$                                      | $v = 3 \dots 12; g(4) = 0.02, g(5) = 0.04,$<br>$g(6) = 0.05, g(7) = 0.10,$<br>$g(8) = 0.14, g(9) = 0.21, g(10) = 0.25,$<br>$g(11) = 0.15, g(12) = 0.06$ |
| 6a              | DF(v) + DF $\rightleftharpoons$ DF(v-1) + DF                                     | $k_{6,v}^{DF} = v^{1.9} (8 \times 10^{14} T^{-1.3} + 1.1 \times 10^{14} T^{2.37})$                  | $v = 1 \dots 13.$   |
| 6b              | DF(v) + M $\rightleftharpoons$ DF(v-1) + M                                       | $k_{6,v}^M = v^{1.9} \times A_M \times 10^{-5} T^{4.5}$   | $A_{Ar} = A_{F_2} = 1.6; A_{He} = 2.5$  |
| 6c              | DF(v) + D $\rightleftharpoons$ DF(v') + D  | $k_{6,v,v'}^D = 4 \times 10^{11} \exp(-2000/RT)$  | $v = 1 \dots 13; v' = 0 \dots (v-1)$  |
| 6d              | DF(v) + F $\rightleftharpoons$ DF(v-1) + F                                       | $k_{6,v}^F = v^{1.9} \times 4 \times 10^{13} \exp(-2700/RT)$  | $v = 1 \dots 13.$   |
| 6e              | DF(v) + HF $\rightleftharpoons$ DF(v-1) + HF                                     | $k_{6,v}^{HF} = v^{1.9} (5.2 \times 10^{14} T^{-1.2} + 135 T^3)$                                    | $v = 1 \dots 13.$   |
| 6f              | DF(v) + D <sub>2</sub> $\rightleftharpoons$ DF(v-1) + D <sub>2</sub>             | $k_{6,v}^{D_2} = v^{1.9} (1.5 \times 10^{11} T^{-1} + 2.5 \times 10^{13} T^{2.28})$                 | $v = 1 \dots 13.$   |
| 7               | DF(v) + DF(v') $\rightleftharpoons$ DF(v+1) + DF(v'-1)                           | $k_{7,v} = g(v) \times 4 \times 10^{15} T^{-1}$   | $g(v) = (v+1)^{0.5}; v \geq v' \geq 1; v = 1 \dots 12.$   |
| 8               | DF(v) + D <sub>2</sub> (v') $\rightleftharpoons$ DF(v+1) + D <sub>2</sub> (v'-1) | $k_{8,v} = g(v) \times 1.6 \times 10^{10} T^{1.5} \exp(407/RT)$                                     | $g(v) = (v+1)^{0.5}; v = 0 \dots 12.$   |
| 9               | D <sub>2</sub> (v) + M $\rightleftharpoons$ D <sub>2</sub> (v-1) + M             | $k_{9,v}^M = 1.5 \times 10^{-6} T^{5.33} \exp(526/RT) v A_M$  | $A_{D_2} = 1; A_F = A_{F_2} = A_{Ar} = 0.2$   |

APPENDIX C. CHANGES IN RATE COEFFICIENTS FOR  $H_2-F_2$  SYSTEM  
FROM 1978 RECOMMENDATIONS OF REFERENCE 4

| Reaction Number | Reaction   | Changes In Rate Coefficients   |
|-----------------|--|--|
| 1a              | $H_2(0) + M_1 \rightleftharpoons 2H + M_1$             | None   |
| 1b              | $H_2(0) + H_2 \rightleftharpoons 2H + H_2$             | None   |
| 1c              | $H_2(0) + H \rightleftharpoons 2H + H$                 | None   |
| 2               | $F_2 + M_2 \rightleftharpoons 2F + M_2$                | None   |
| 3               | $HF(v) + M_3 \rightleftharpoons H + F + M_3$           | Larger by 10%.   |
| 4a              | $F + H_2(0) \rightleftharpoons HF(v) + H$              | Larger by 50% at 300K, within 15% at 1000-2000K; distribution remains the same.  |
| 4b              | $HF(v) + H \rightleftharpoons H_2(v') + F$             | Increased by a factor of 35 for $v = 4$ , a factor of 8 for $v = 5$ , and a factor of 6 for $v = 6$ .  |
| 5               | $H + F_2 \rightleftharpoons HF(v) + F$                 | Smaller at 300K by a factor of 2.3, larger at 2000K by factor of 2.7.  |
| 6a              | $HF(v) + HF \rightleftharpoons HF(v-1) + HF$           | Single quantum instead of multiquantum, larger at high $v$ .   |
| 6b              | $HF(v) + H_2 \rightleftharpoons HF(v-1) + H_2$         | Smaller by factor of 3 at 300K, larger by 15% at 1000K, $v^{2.7}$ instead of $v$ dependence. Inverse T dependence of low T: $T^{-2.25}$ instead of T dependence at high T. |
| 6c              | $HF(v) + M_4 \rightleftharpoons HF(v-1) + M_4$         | Larger by 50% at 300K, smaller by 20% at 1000K, $v^{2.7}$ instead of $v$ dependence.   |
| 6d              | $HF(v) + H \rightleftharpoons HF(v') + H$              | Slower by factor of 4 for $v = 1$ , factor of 7 for $v = 2$ .  |
| 6e              | $HF(v) + H \rightleftharpoons HF(v-1) + H$             | Factor of 3 slower at 300K and 27 slower at 1000K for $v = 3$ .  |
| 6f              | $HF(v) + F \rightleftharpoons HF(v-1) + F$             | Larger by 6%, $v^{2.7}$ instead of $v$ dependence.   |
| 6g              | $HF(v) + DF \rightleftharpoons HF(v-1) + DF$           | Same between 300 and 1000K, $v^{2.7}$ scaling instead of $v^{-1}$ , single quantum instead of multiquantum.  |
| 7               | $HF(v) + DF(0) \rightleftharpoons HF(v-1) + DF(1)$     | Same at 295K, smaller by factor of 3.3 at 1000K, $v^{2.7}$ scaling instead of $v$ .  |
| 8               | $HF(v) + HF(v') \rightleftharpoons HF(v+1) + HF(v'-1)$ | Larger by factor of $v(v+1)^{0.35}$ ; 25% for $v = 1$ , factor of 2.9 for $v = 2$ , factor of 4.9 for $v = 3$ .  |
| 9               | $HF(v-1) + H_2(1) \rightleftharpoons HF(v) + H_2(0)$   | Larger by 16% at 1000K, same at 300K, $v^{0.35}$ scaling instead of $v$ , $T^{0.5}$ instead of $T^0$ .   |
| 10              | $HF(v) + N_2(0) \rightleftharpoons HF(v-1) + N_2(1)$   | Unchanged within 10% between 300 and 1000K, $v^{2.7}$ scaling instead of $v$ .   |
| 11a             | $H_2(v) + M_5 \rightleftharpoons H_2(v-1) + M_5$       | None   |
| 11b             | $H_2(v) + H \rightleftharpoons H_2(v-1) + H$           | None   |

**APPENDIX D. CHANGES IN RATE COEFFICIENTS FOR  $D_2$ - $F_2$  SYSTEM  
FROM 1977 RECOMMENDATIONS OF REFERENCE 2**

| Reaction Number | Reaction   | Changes in Rate Coefficients  |
|-----------------|--|---|
| 1a              | $2D + Ar \rightleftharpoons D_2 + Ar$                    | None  |
| 1b              | $2D + D \rightleftharpoons D_2 + D$                      | None  |
| 1c              | $2D + D_2 \rightleftharpoons D_2 + D_2$                  | None  |
| 2               | $F_2 + M \rightleftharpoons 2F + M$                      | None  |
| 3               | $DF(v) + M \rightleftharpoons D + F + M$                 |   |
| 4a              | $F + D_2(0) \rightleftharpoons DF(v) + D$                | Overall k approximately the same at 300 K, smaller by a factor of $\approx 2$ at 1000-2000 K. Distribution remains the same (however the expression in Table A-1 of Ref. 2 contains some typographic errors). |
| 4b              | $DF(v) + D \rightleftharpoons F + D_2(v')$               | k decreases with v rather than being v-independent.   |
| 5               | $D + F_2 \rightleftharpoons DF(v) + F$                   | Smaller by 30% at 300K, larger by a factor of 3.6 at 2000K, g(v) shifted toward higher v.   |
| 6a              | $DF(v) + DF \rightleftharpoons DF(v-1) + DF$             | Same for v = 1, somewhat smaller for v $\geq 2$ .   |
| 6b              | $DF(v) + M \rightleftharpoons DF(v-1) + M$               | 30% smaller at 300 K; unchanged at 1500 K for Ar, $F_2$ .<br>50% larger at 300 K; unchanged at 1500 K for He. Steeper v - dependence.   |
| 6c              | $DF(v) + D \rightleftharpoons DF(v') + D$                | 20% smaller for v = 1, factor of 20 smaller for other v.  |
| 6d              | $DF(v) + F \rightleftharpoons DF(v-1) + F$               | Factor of 2.4 faster at 300K for v=1; scaling changed from v' to v <sup>1.9</sup> ; single quantum instead of multiquantum.   |
| 6e              | $DF(v) + HF \rightleftharpoons DF(v-1) + HF$             | Same for v = 1, g(v) changed to v <sup>1.9</sup> from v <sup>2.2</sup> .  |
| 6f              | $DF(v) + D_2 \rightleftharpoons DF(v-1) + D_2$           | 30% larger at 295K and 16% smaller at 1000K, g(v) changed to v <sup>1.9</sup> from v. Inverse T dependence at low T; T <sup>-2.28</sup> instead of T <sup>-2.4</sup> dependence at high T.                    |
| 7               | $DF(v) + DF(v') \rightleftharpoons DF(v+1) + DF(v'-1)$   | Same for v = 1, factor of 2 larger for v = 2. (v+1) <sup>0.5</sup> instead of (1.8) <sup>1-v</sup> dependence.  |
| 8               | $DF(v) + D_2(v') \rightleftharpoons DF(v+1) + D_2(v'-1)$ | 10% larger at 300K and 20% larger at 1000K, g(v) changed to (v+1) <sup>0.5</sup> from (v+1).  |
| 9               | $D_2(v) + M \rightleftharpoons D_2(v-1) + M$             | None  |

# APPENDIX E. CURRENT STATUS IN UNCERTAINTIES IN HF AND DF KINETICS

| REACTIONS  | HF SYSTEM  | DF SYSTEM  |
|--|--|--|
| <b>I. PUMPING REACTIONS</b>  |  |  |
| A. $F + H_2(D_2)$ Overall rate   | $200 \leq T \leq 800$ : $\pm 25\%$<br>$800 \leq T \leq 2000$ : $\pm 60\%$<br>$T \approx 300$ : $\pm 10\%$<br>$T > 500$ : $\pm 30\%$  | $200 \leq T \leq 800$ : $\pm 25\%$<br>$800 \leq T \leq 2000$ : $\pm 60\%$<br>$T \approx 300$ : $\pm 15\%$<br>$T > 500$ : $\pm 30\%$  |
| Vibrational distribution of product  |  |  |
| B. $H(D) + F_2$ Overall Rate   | $200 \leq T \leq 800$ : $\pm 60\%$<br>$800 \leq T \leq 1500$ : Factor of 2<br>$T \approx 300$ : $\pm 20\%$<br>$T > 500$ : $\pm 40\%$   | $200 \leq T \leq 800$ : $\pm 60\%$<br>$800 < T \leq 1500$ : Factor of 2<br>$T \approx 300$ : $\pm 50\%$<br>$T > 500$ : Factor of 2   |
| Vibrational Distribution of Product  |  |  |
| <b>II. DISSOCIATION-RECOMBINATION REACTIONS</b>  |  |  |
| A. $F_2 + M = 2F + M$  | $M = He$ $T = 300$ : Factor of 1.5 - 2<br>$M = Ar, F_2$ $T = 300$ : Larger uncertainty<br>Other M, other T: Large uncertainty  |  |
| B. $H_2(D_2) + M = 2H(D) + M$  | $M = H_2$ $T \leq 300$ : $\pm 60\%$<br>$T \approx 1000$ : Factor of 2<br>$M = H$ $T \geq 300$ : Factor of 3<br>$M = Ar, N_2$ All T: Factor of 2<br>Other M, All T: Factor of 3 - 10<br>$M = Ar$ , $T \geq 3000$ : Factor of 2<br>$T \leq 1000$ : Factor of 5<br>Other M, All T: Factor of 3 - 5  | $M = D_2$ $T \leq 300$ : $\pm 60\%$<br>$T \approx 1000$ : Factor of 2<br>$M = D$ $T \geq 300$ : Factor of 5<br>Other M, All T: Factor of 5 - 10<br>All M, all T: Factor of 3 - 10                        |
| C. $HF(DF) + M = H(D) + F + M$   |  |  |
| <b>III. V-V ENERGY TRANSFER</b>  |  |  |
| A. $HF(v) + HF(v') = HF(v'') + HF(v''')$<br>$DF(v) + DF(v') = DF(v'') + DF(v''')$  | $v = v' = 1$ $T \approx 300$ : $\pm 40\%$<br>$T > 500$ : $\pm 60\%$<br>Other v, v', Any T: Factor of ~2<br><b>ASSUMPTION OF <math>\Delta v = 1</math> HAS NOT BEEN VERIFIED EXPERIMENTALLY</b>   | $v = v' = 1$ $300 \leq T \leq 750$ : $\pm 40\%$<br>$1000 \leq T$ : $\pm 60\%$<br>Other v, v', Any T: Factor of ~2<br><b>ASSUMPTION OF <math>\Delta v = 1</math> HAS NOT BEEN VERIFIED EXPERIMENTALLY</b> |
| B. $HF(v) + H_2(0) = HF(v'') + H_2(v''')$<br>$DF(v) + D_2(0) = DF(v'') + D_2(v''')$  | $v = 1 - 3$ , $T \approx 300$ : $\pm 50\%$<br>Other v, any T: Factor of ~2<br><b>ASSUMPTION OF <math>\Delta v = 1</math> HAS NOT BEEN VERIFIED EXPERIMENTALLY</b>  | $v = 1 - 4$ , $T \approx 300$ : $\pm 50\%$<br>Other v, any T: Factor of ~2<br><b>ASSUMPTION OF <math>\Delta v = 1</math> HAS NOT BEEN VERIFIED EXPERIMENTALLY</b>  |
| <b>IV. V-R, T ENERGY TRANSFER</b>  |  |  |
| A. SELF-RELAXATION:<br>$HF(v) + HF$<br>$DF(v) + DF$  | $v = 1$ , $200 \leq T \leq 3000$ : $\pm 30\%$<br>$v > 1$ , Any T: Factor of 1.5 - 2  | $v = 1$ , $200 \leq T \leq 700$ : $\pm 40\%$<br>$v > 1$ , Any T: Factor of 1.5 - 2   |
| B. DEACTIVATION BY H(D) ATOMS  | $v = 1, 2$ , $200 \leq T \leq 300$ : $\pm 25\%$<br>$v \geq 3$ , Any T: Factor of 5 - 10<br><b>LARGE UNCERTAINTY IN VIBRATIONAL DISTRIBUTION OF PRODUCT HF(DF)</b>  | $v = 1$ , $T = 300$ : Factor of 3<br>$v \geq 2$ , Any T: Factor of 5 - 10<br><b>LARGE UNCERTAINTY IN VIBRATIONAL DISTRIBUTION OF PRODUCT HF(DF)</b>  |
| C. DEACTIVATION OF $HF(DF)^a$ BY $DF(HF)$<br><sup>a</sup> (includes possible v-v contribution)   | $v = 1$ , $300 \leq T \leq 1000$ : $\pm 50\%$<br>$v > 1$ , Any T: Factor of 2 - 3  | $v = 1$ , $300 \leq T \leq 750$ : $\pm 30\%$<br>$v > 1$ , Any T: Factor of 2 - 3   |
| D. DEACTIVATION BY Ar, He, $N_2$   | $v = 1$ , $1000 \leq T$ : $\pm 50\%$<br>$v > 1$ , Any T: Factor of 2   | $v = 1$ , $1000 \leq T$ : Factor of 2<br>$v > 1$ , Any T: Factor of 3  |
| E. DEACTIVATION BY F ATOMS   | $v = 1$ , $T = 300$ : $\pm 50\%$<br>$v = 1$ , $T > 1000$ : Factor of 3<br>$v > 1$ , Any T: Factor of 2 - 3   | $v = 1$ , $T = 300$ : $\pm 50\%$<br>$v = 1$ , $T > 1500$ : Factor of 2<br>$v > 1$ , Any T: Factor of 2 - 3   |
| F. DEACTIVATION BY OTHER CHAPERONES  | Measurements have been reported for $v = 1$ , $T = 300$ , for numerous stable chaperones, and correlation rules have been proposed. Uncertainties in general are approximately a factor of 2. For $T \neq 300$ and/or $v > 1$ the uncertainties are larger. Also, for free radical chaperones (e.g., NF, NF <sub>2</sub> , CF <sub>3</sub> , SF <sub>3</sub> , etc.) uncertainties are larger. |  |
| <b>V. ROTATIONAL RELAXATION</b>  |  |  |
| Order of magnitude uncertainty for low j ( $\leq 8$ ), owing to disagreement between theory and experiment, and also to ambiguities in interpretation of experimental data. Larger uncertainty for $j > 8$ owing to lack of any experimental data. |  |  |

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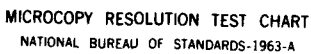
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TR-0083(3603)-2  
Dated 25 October 1982

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SUBJECT: Revision, pages 22 and 23

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The attached paragraph replaces the paragraph beginning on the bottom of page 22, following Table 3, and continuing to the end of page 23.

A comparison of the methods and results with theoretical calculations<sup>37</sup> (which predict that DF is formed only in  $v = 5$  through 9, peaking at  $v = 8$ ) suggests that the results of Jonathan et al.<sup>40</sup> give a distribution slightly too broad, perhaps because of secondary reactions. On the other hand, the results of Bittenson et al.<sup>29</sup> imply that the  $D + F_2$  reaction is significantly more efficient at converting chemical to vibrational energy than is the  $H + F_2$  reaction — or any other analogous halogen reaction. Because there is no good explanation for such a discrepancy, we are reluctant to base a recommendation on those results. Our recommendation is based on the findings of Jonathan et al., narrowed somewhat to take into account the theoretical prediction that no energy goes into low vibrational levels. The recommended room-temperature distribution numbers are:  $k_6(4) \dots k_6(12) = 0.02, 0.04, 0.05, 0.10, 0.14, 0.21, 0.25, 0.15, 0.06$ .